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Risk assessment of Pursiala groundwater area in poor chemical state

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Giacomo Ciavatti

Thesis supervisor:	Jaana Sorvari
Thesis co-supervisor:	Mette Broholm
Thesis instructor:	Sirkku Tuominen

Aalto University
School of Engineering

Aalto University, P.O. BOX 11000, 00076 AALTO
www.aalto.fi
Abstract of master's thesis

Author: Giacomo Ciavatti

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Supervisor: Jaana Sorvari

Co-supervisor: Mette Broholm

Instructor: Sirkku Tuominen

Abstract

The population in Finland relies heavily on the aquifers as a source of potable water. The aim of the project was to understand if the industrial activities have caused a deterioration of the groundwater quality of the Pursiala aquifer and to study if the use of groundwater at Pursiala may cause significant health risks to the local people. The literature review focused on some methods used to manage a contaminated site/groundwater and on the characteristics of the chemicals of interest. The Master's Thesis dealt with two areas around a sawmill and a wood impregnation plant, which, respectively, have caused a discharge of chlorophenols (CPs) and polycyclic aromatic hydrocarbons (PAHs) in the groundwater. The study of the aquifer vulnerability was conducted with the DRASTIC method, which gives as result the DRASTIC vulnerability index (DVI). As a result, the higher is the index, the higher is the vulnerability. The maximum DVI values of 175.9 (CPs) and 180.2 (PAHs) indicate that the aquifer is very vulnerable. The dispersion of the contaminants in the aquifer was analyzed using a Danish preliminary risk assessment tool named GrundRisk. Monitoring data collected from years 2004-2013, for each chemical detected in the source area in the aquifer, were considered for the simulations in GrundRisk. In the case of PAHs, the simulations showed an excess of the groundwater guidelines (for drinking-water) at the point of compliance for only benzo(a)pyrene. The assessment of risks caused by CPs was based on the concentrations detected in the groundwater monitoring wells located in the sawmill area. All the concentrations were above the groundwater guidelines. Based on these results, a human health risk assessment was executed on the two groups of chemicals. The sum of the Hazard Quotients HQs gave a maximum Hazard Index HI of 460.1 and 54.3 for, respectively, CPs and PAHs. To summarize, the DRASTIC method and the GrundRisk tool showed the high vulnerability of the Pursiala aquifer and the negative impact of the industrial activities on the groundwater quality. Because the acceptable level for non-carcinogenic risks is HI=1, the industrial activities cause a threat to human health. It is therefore recommended to execute further investigations and remedial actions. Lastly, the simulations gave almost similar concentrations than those documented in the POVET database, which shows that GrundRisk is applicable to the preliminary risk assessment of groundwater contamination.

Keywords: Aquifer vulnerability, contamination, groundwater modelling, groundwater quality, human health, risk assessment

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Ad maiora

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Symbols and abbreviations

Symbols

A	Source area
α_l	Longitudinal dispersivity in the x direction
α_t	Transversal dispersivity in the y direction
α_v	Vertical dispersivity in the z direction
C_c	Contaminant concentration
C_0	Source concentration of the contaminant
D_{Dermal}	Dermal exposure dose
$D_{Ingestion}$	Ingestion exposure dose
D_x	Longitudinal dispersion coefficient
D_y	Transversal dispersion coefficient
D_z	Vertical dispersion coefficient
f_{oc}	Weight fraction of organic carbon in the soil
I	Infiltration flux
J	Mass flux
K_a	Dissociation constant
K_d	Distribution coefficient
K_{oc}	Distribution coefficient between a chemical and the soil organic carbon
K_{ow}	Octanol Water partition coefficient
L	Length
L_x	Length of the contaminant source in the x direction
L_y	Length of the contaminant source in the y direction
λ	First order degradation rate of the chemical
M	Mass
M_d	Mass discharge
n	Porosity
N_p	Number of DRASTIC parameters
P	Dermal permeability coefficient
P_r	Rate of parameter
P_w	Weight of parameter
R	Retardation coefficient
ρ_b	Bulk density
T	Time
$t_{1/2}$	Half-life
u	Groundwater velocity
W	Effective weight
ϕ_n	Neutral fraction
z	Depth

Abbreviations

A	Aquifer media
AF	Absorbed fraction
AT	Averaging Time
BSA	Body Surface Area
BW	Body Weight
C	Hydraulic conductivity
CF	Conversion Factor
CP	Chlorophenol
DCP	Dichlorophenol
D	Depth to water table
DNAPL	Dense Non Aqueous Phase Liquid
DVI	Drastic Vulnerability Index
ED	Exposure duration
EF	Exposure factor
ELY	Centre for Economic Development, Transport and the Environment
EPA	Environmental Protection Agency
ET	Exposure Time
F	Frequency of exposure
GI	Gastrointestinal factor
I	Impact of vadose zone
IR	Intake Rate
HI	Hazard Index
HQ	Hazard Quotient
IRIS	Integrated Risk Information System
ISCO	In Situ Chemical Oxidation
NOD	Natural Oxidant Demand
PAH	Polycyclic Aromatic Hydrocarbon
PCP	Pentachlorophenol
POC	Point Of Compliance
R	Net recharge
RfD	Reference Dose
SA	Source Area
SI	Sensitivity Index
S	Soil media
STDV	Standard Deviation
SYKE	Finnish Environmental Institute
T	Slope
TeCP	Tetrachlorophenol
TCP	Trichlorophenol
UCL	Upper Confidence Limit

1. Introduction

1.1 Groundwater as a resource

Since the beginning of the 20^{th} century, the impact of the industrial activities on nature has largely increased the necessity of finding efficient solutions for the preservation of the natural resources [1]. The contamination of natural resources can have side effects for the living beings. When a case of contamination is discovered, it is necessary to determine all the risks to human beings and biota [2]. The typical procedure adopted is called risk assessment, which determines the human and the environmental consequences due to a contamination. The outcomes of the risk assessment are different according to the environmental medium taken into account (e.g. air, soil or water). This project was focused on a natural resource, which is not only important in Finland, but nowadays is considered as one of the most important resources of the world: groundwater [3].

Generally, groundwater is the water found underground, it is stored inside and moves slowly through a geologic formation called aquifer, i.e. an underground body of soil through which the water flows [4]. An aquifer can be confined, i.e. between two permeable layers with the groundwater under pressure that will rise in a borehole above the bottom of the confining layer, or unconfined, i.e. where the open pore space of the overlying soil brings the groundwater in direct contact with the atmosphere [5]. Figure 1.1 visualizes the differences between the two types of aquifers.

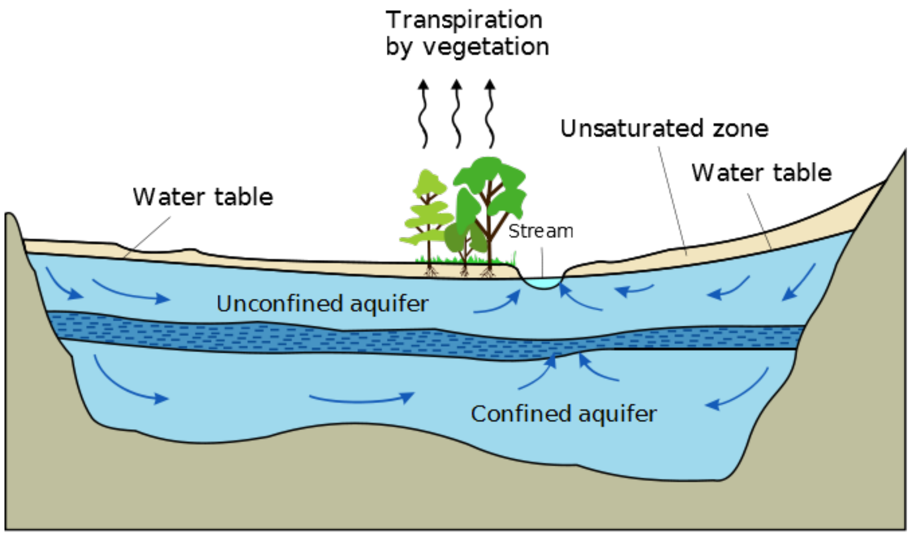


Figure 1.1: Confined and unconfined aquifers [6]

There are many reasons to consider the study of the groundwater vulnerability essential. In particular, in 2006, the directive of the European parliament stated that groundwater is a valuable source that must be protected from any kind of contamination and deterioration [7]. In addition, it is estimated that almost one-third of the global population relies on groundwater as an important source for water supply. The data collected from the European Economic Association (EEA) and the United Nations Economic Commission for Europe (UNECE), about the usage of groundwater in Europe for drinking water supply, confirmed this growing trend (see Figure 1.2).

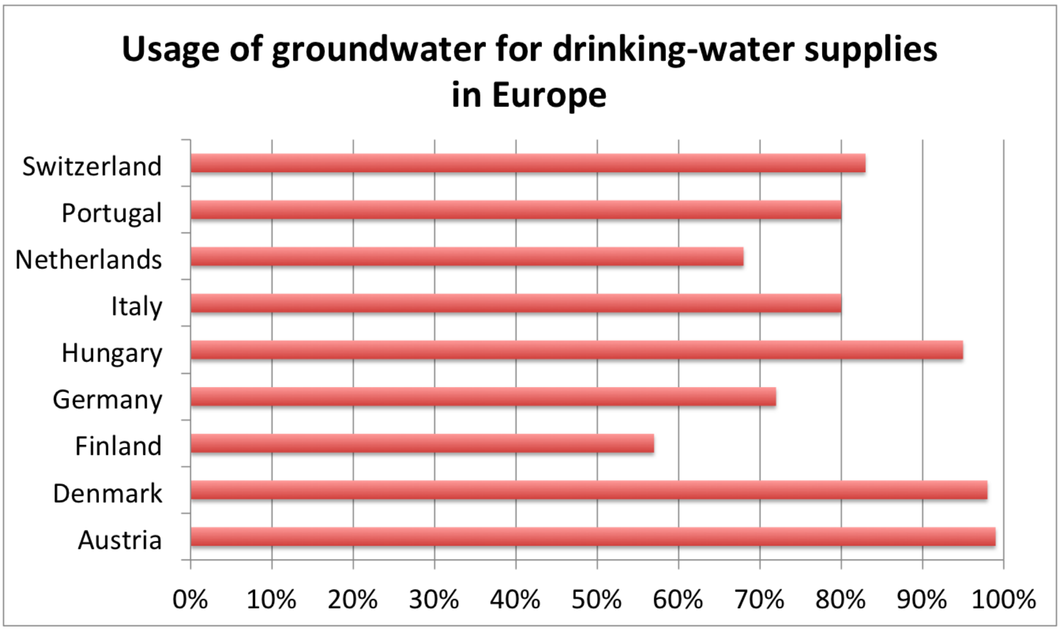


Figure 1.2: Usage of groundwater for drinking-water supplies in Europe [8, 9]

Because groundwater contamination represents a serious threat to water supply, it is necessary to monitor the quality of groundwater areas. Normally, the human activities are monitored because their probability of contamination is quite high (e.g. industrial activities) [10]. This means that, even if the groundwater is in a good status, the competent authority must continuously supervise its characteristics [11].

1.2 Groundwater monitoring

The monitoring procedures vary according to the country. Considering Finland, the monitoring stations of the Finnish Environmental Institute (SYKE) are consulted by the local authority. All the stations are located in areas where there is little human activities and the quality of groundwater represents "the natural state" of groundwater [11]. The monitoring locations vary according to the case and site information like the hydrogeological conditions or the possible use of the groundwater area (e.g. water supplies) [7]. The Finnish groundwater monitoring covers 80 groundwater observation stations distributed along the country [12]. They are located in different areas (their size is between 0.2 and 3 km^2), which vary according to the soil and climatic characteristics [13]. SYKE is responsible for coordinating the groundwater sample (generally from 2 to 4 times a year), which are collected at ELY Centres' laboratories, i.e. the Centres for Economic Development, Transport and the Environment [12].

Groundwater areas can be subjected to monitoring related to environmental permits. These operations are normally executed in areas where human activities are located (e.g. landfills, industrial plants or service stations) [11]. The scope and content of these monitoring operations are case-specific and are established by the ELY Centres [11].

The monitoring operations must include an estimate of the environmental impact of the human activities. Therefore, by taking into account the environmental conditions of the area and the activity itself, the authority assesses the adequacy of the number & the frequency of water samplings and the range of substances that have to be monitored [11]. If necessary, a wider sampling operation is executed to further clarify the general state of groundwater [11].

If some groundwater body or classified groundwater area is suspected to be contaminated by human activities, operators like companies or industrial plants usually hire a consulting company for executing studies in the area [11].

1.3 Finnish aquifers

About 60% of the drinkable water distributed by the Finnish communal and private water works derives directly from natural or artificial groundwater [14]. The Finnish groundwater formations have some common characteristics [10]:

- they are mainly situated in eskers and endmoraines;
- they have a thickness of around 10 meters;
- the groundwater depth below the surface is normally between 2 and 5 meters.

According to the legislation of February 2015, on protecting groundwater, more than 6000 groundwater areas were classified in Finland [15]. The most important are restricted to the QuateAssessment of chemical risks to groundwater qualityrnary deposits [10], which mainly consist of permeable sand, gravel, glacial and deglacial deposits, with the the last two covering almost 7% of Finland [14]. These aquifers are ranked at the top among the best reserves of groundwater [15]. The aquifers in Southern Finland are in sandy and gravelly eskers, as well as in the Salpausselkä ice-marginal end moraine deposits, i.e. an extensive ridge system formed during the ice age in Southern Finland [10]. Figure 1.3 shows details of the quaternary gravel and sand deposits and the three Salpausselkä formations.

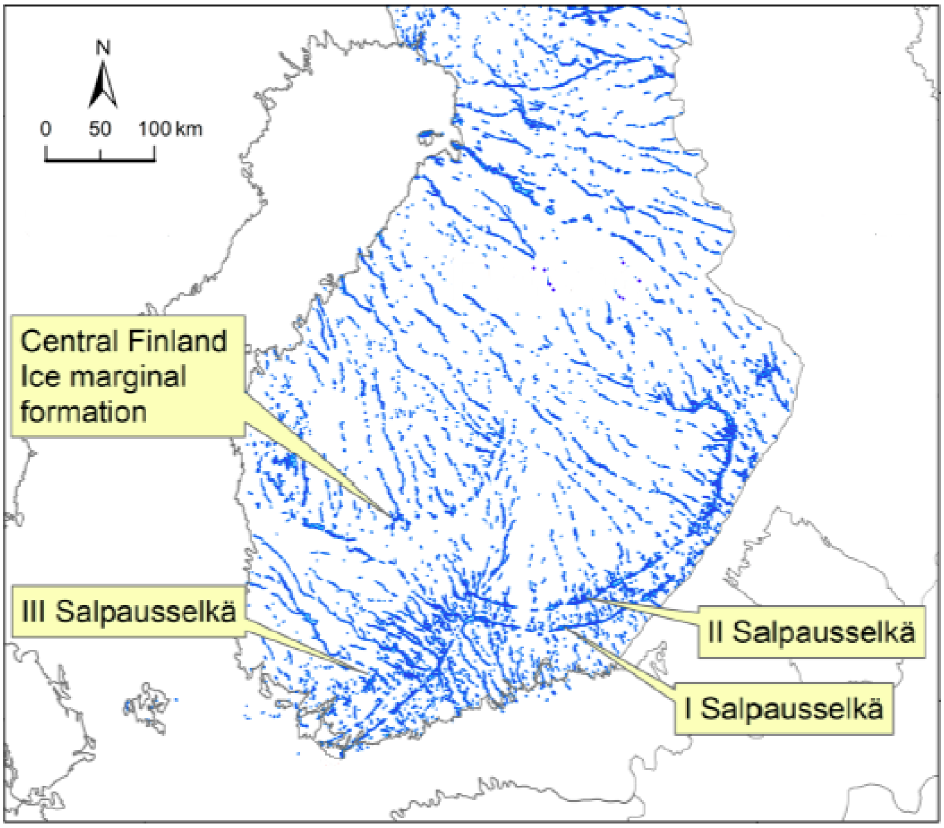


Figure 1.3: Quaternary gravel and sand deposits (highlighted in blue), together with the three Salpausselkä formations [16]

1.4 Finnish risk assessment practices of contaminated land

The procedures that are normally adopted in a groundwater risk assessment aim at providing information regarding the aquifer vulnerability and the impact of the chemicals on the groundwater quality. In Finland, there is no clear recommendation about a groundwater risk assessment for contaminated sites. Generally, when a risk assessment is conducted in Finland, the first step consists in identifying all the chemicals of potential concern (COPCs), i.e. all those chemicals that may represent a risk for human beings or biota. The concentrations detected in an area are compared with all those concentrations that are believed to not produce any health risk (benchmarks) [17]. Once the source has been analyzed and the COPCs are known, generally a conceptual model is drawn in order to visualize the problems and show the contamination pathways together with the receptors (see Figure 1.4) [2]. This represents the basis of the risk assessment procedure.

Figure 1.4: Simplified illustration of the formation of the risks [2]

The risk assessment can have different dimensions (in time and in space), it can differ if related to human health or the environment and it can have diverse levels: qualitative, i.e. a simple descriptive estimate of risks, and quantitative, which produces numeric risk estimates [2]. It can be:

- **Deterministic**, i.e. the risk is estimated by considering only one type of scenario for a contamination problem [18];
- **Probabilistic**, i.e. the risk is estimated by considering all the possible variabilities and uncertainties, e.g. the lack of knowledge or problems connected to the computational method used (wrong data or invalid model) [19]. In comparison to the deterministic approach, the probabilistic produces a distribution of risk estimates by considering all the possible scenarios for a contamination problem [18].

If processes like degradation or transformation of the contaminants (i.e. all the phenomena happening in the soil) are taken into account, the approach is realistic [19]. It is not possible to state if the deterministic procedure is more efficient than the probabilistic [18]. The choice is related to the contamination problem. The nature of the risks, the purpose of the analysis and the available data and resources will tell what is the more convenient procedure to use [19]. For most of risk assessments, the deterministic approach is preferred because it is free of all the typical uncertainties of the probabilistic approach (e.g. the quality of the input data) [18].

The knowledge on the contaminants and their exposure pathways allows determining the risk for a specific target group. If the assessment is developed on human beings, this process is called human health risk assessment, i.e. the determination of the potential risks that human beings might face when exposed to a contaminant [20]. One of the most common procedures is the calculation of the hazard quotient (HQ) [21]. By definition, the hazard represents a harmful agent that can cause damage to the the environment or to humans [22]. The acceptable level for the Hazard Quotient, i.e. no adverse affect is likely to occur, is for HQ equal to 1 [22]. If the contamination is due to the contribution of more than one substance, the risk is insignificant if the sum of the contaminant-specific HQs (i.e. the Hazard Index HI) is below 1 [21].

1.5 Approach and goal of the project

The case study presented in this Master's Thesis was focused on one of the most important groundwater areas in Southern Finland: the Pursiala aquifer (see Figure 1.5), which is located nearby the city of the subregion Etelä-Savo named Mikkeli, at approximately 61º41′N 27º16′E.

The studies conducted on the groundwater quality of the Finnish aquifers are limited. In particular, no scientific study has been conducted in Pursiala to assess the groundwater quality and its possible deterioration due to the industrial activities. Therefore, the goal of the Master's Thesis was to provide information for the risk management of the Pursiala groundwater area and to broaden the focus of groundwater risk assessments in Finland. The thesis was divided in three parts.

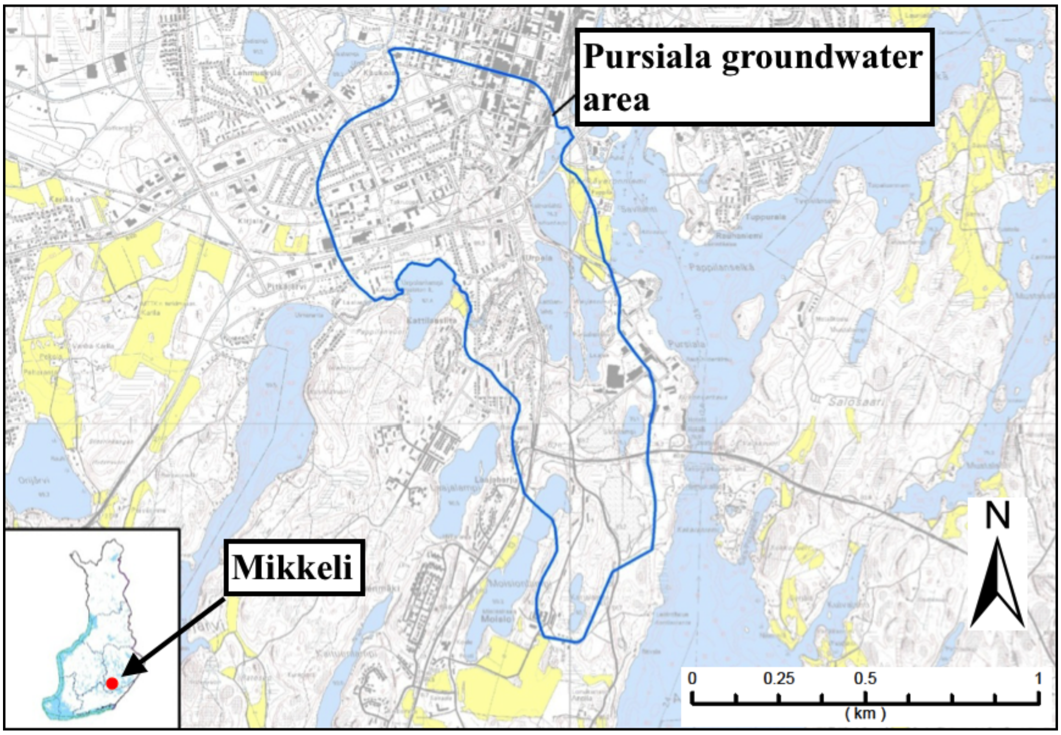


Figure 1.5: Pursiala groundwater area [23]

The first part of this thesis consists of a literature review of tools used for the study of the aquifers' vulnerability and the dispersion of the contaminants in an aquifer (see Chapter 2). The main models used in previous studies were considered and the outcomes of some scientific articles were analyzed. Due to the large number of groundwater modelling tools, it was decided to focus only on those tools that were more relevant to this project and more common in the scientific articles. It follows a description of the principal physical characteristics of the chemicals detected in the areas of interest (see Chapter 3). The chemicals of potential concern (COPCs) were identified by using the monitoring stations of the Finnish groundwater database named POVET and by comparing the concentrations with the groundwater benchmarks (see Chapter 4).

The second part of the thesis focuses on the methods on which the Master's Thesis was developed. The first analysis was conducted on the Pursiala aquifer's vulnerability, in order to describe how much it is easy, or hard, for a contaminant to reach an aquifer (see Chapter 5.1). The impact of the COPCs on the groundwater quality was then modelled with a groundwater modelling tool tool (see Chapter 5.2).

Lastly, in order to get an idea on the health risk for the local people of Mikkeli, a human health risk assessment was executed (see Chapter 5.3). The calculations executed in this part were very basic because, as said previously, the focus of the Master's Thesis was mainly on the groundwater risk assessment. The results were evaluated and conclusions were drawn about the reliability of the procedures and whether they can be applied in other groundwater situations (see Chapter 6).

2. Assessment of chemical risks to groundwater quality

The chapter aims at describing some typical methods that are used to study the vulnerability of the aquifer and to predict the behavior of the contaminants in an aquifer, and at introducing the methods that were used in the Master's Thesis.

2.1 Vulnerability appraisal

Many approaches have been developed to study the vulnerability of the aquifer, and generally it is possible to identify three different types of procedures.

The first approach is the process-based method, which allows studying the migration of the contaminants by using simulation models. The problems derive from the complexity of the computation and the lack of information available (some of the data necessary for the computation might be restricted) [24]. The second method is a statistical approach: basically the relationship between the spatial variables and the groundwater contaminants are determined, but problems might arise if there are not enough observations and if there are doubts about, for example, the most suitable variables for the approach or the data accuracy [25]. The last approach is the overlay-index method, which is built according to the weights, ranges and ratings of the typical characteristics of the aquifer. The result of the method is an index which contains information about the vulnerability of the aquifer [26]. Among the three methods, the third procedure is normally the preferred one because it is very simple and allows managing a large amount of data [27].

A study on the vulnerability of the aquifer was executed by Kumar et al. [28] through the SINTACS method [29]. By estimating the so-called SIVI index, it is possible to identify the areas of an aquifer that are most vulnerable to the groundwater contamination. The index is calculated by seven parameters, which contain the hydrogeological information of the aquifer. Each parameter has a weight and a rating, which depend, respectively, on the importance of the parameter in the model and on the value of the parameter itself. The SINTACS method is integrated with GIS tools to produce maps that show the variation of the index along the area analyzed. The study conducted by Kumar et al. was about a contamination problem caused by nitrate in an Indian aquifer. After obtaining the information on how the SIVI index varied in the aquifer, the nitrate concentrations were compared with the index and the most vulnerable area of the aquifer were assessed [28]. This means that, in order to be successful with the SINTACS method, it is necessary to have information on the hydrogeological characteristics of the area.

Another method adopted for studying the vulnerability of the aquifer is the DRASTIC method [30]. It has the same characteristics of the SINTACS method. The DRASTIC method is in fact the American version of SINTACS, which is mostly used to assess the groundwater contamination in the Mediterranean [31]. Just like SINTACS, through the hydrogeological characteristics of the area, which are grouped in seven parameters, the

DVI index is produced to determine the vulnerability of the aquifer. The higher is the index the more vulnerable is the aquifer. The parameters considered for the DRASTIC and the SINTACS index are exactly the same, but have only small differences in their rates and weights. If DRASTIC is able to determine the vulnerability of the aquifer due to contamination via source from the groundwater, SINTACS have more options related to the contamination of watercourses connected to the aquifer (e.g. lakes and rivers) [32]. Gupta [33] used the DRASTIC method to study the vulnerability of an Indian region. All the areas that need to be monitored due to their high vulnerability were highlighted, but no comparison was elaborated between the vulnerability indexes and the chemicals in the area because there was no information about them [33]. Jafari and Nikoo [34] proposed the DRASTIC method to study the vulnerability of an Iranian aquifer to nitrate contamination. The procedure was very similar to the one used by Gupta but, in this case, the correlation between the chemicals and the vulnerability indexes was found. In addition, the DRASTIC method was optimized through a sensitivity analysis proposed by Lodwick et al. [35] and by Napolitano and Fabbri [36] in order to obtain a better understanding of the DRASTIC parameters and the role they have in the vulnerability of the aquifer. As a consequence, through this analysis, the correlation between the DVI indexes and the nitrate concentrations, revealed in the area, becomes more precise.

2.2 Models to study contaminant dispersion

Many tools have been developed to study the contaminants' dispersion in an aquifer. In a study conducted by Artimo et al. [37], elevated concentrations of contaminants were detected in an aquifer located in Western Finland. The groundwater flow in the area was modelled using a software named MODFLOW, i.e. a 3-D model developed by USGS (United States Geological Survey) in 1984, which allows simulating groundwater problems in many different conditions (e.g. steady state flow or confined and unconfined aquifer) [38]. To get correct simulations with MODFLOW, detailed information on the study area needs to be collected (e.g. topography, water level, precipitation or evapotranspiration values). In Artimo case, no simulation was executed on the contaminants' transport. The goal of that project was to simulate the flow system and to provide useful information for developing water intake operations in unpolluted parts of the aquifer [37]. Purjenaie et al. [39] used MODFLOW to predict the variation of drawdown in an Iranian aquifer under different pumping operations [39]. MODFLOW has many diverse functionalities. It does not only simulate the groundwater level and flow pattern but, if applied together with other tools, simulates the contaminant transport (e.g. with MT3D) or the particle tracking (e.g. with MODPATH). MODFLOW was implemented by Artimo [40] to study the contamination by tetrachloroethylene in a Finnish aquifer named Honkala, which is in southwestern Finland. After building the groundwater flow model with MODFLOW, MT3D and MODPATH were implemented for, respectively, modelling the tetrachloroethylene concentrations in the aquifer and for simulating the movement of the particles along the groundwater flow path [40]. Saghravani and Mustapha [41] used a package of MODFLOW named Visual MODFLOW to predict the dispersion of phosphorus pollution in un unconfined aquifer [41]. These articles proved that MODFLOW is a very precise software due to the large amount of information inserted in the model and the variety of outcomes that can be produced. This aspect is at the same time a limitation because, as said previously, it needs a highly detailed study of the area. Therefore, the usage of MODFLOW may encounter problems in situations where these information on the area are missing.

Simplified softwares are considered for modelling groundwater contamination. A very simple software used to simulate the natural attenuation of contaminants is called Bioscreen. It is normally applied to describe the release of BTEXs (i.e. benzene, toluene, ethylbenzene and xylene) in petroleum sites [42].. The goal of the software is to model the migration of the plume from the source zone in sites where no engineering operation are executed to reduce the source area. As an output, it is possible to say if only the natural attenuation is suitable for the site or if it is necessary to apply other remediation technologies [42]. Natural attenuation can be modelled with no degradation, a first-order degradtion or an instantaneous biodegradation. The biodegradation of BTEXs is regulated by the presence of electron acceptors at the site. The ones considered in the software are oxygen, nitrate, ferrous iron, methane and sulfate. Therefore, the software can work correctly if the distribution of these electron acceptors is known. Due to its simplicity and efficiency in describing the natural attenuation, Bioscreen was developed in many different case studies. The software was used to analyze the natural attenuation of BTEX compounds at a gas station in California and to check if the remediation of these chemicals through natural attenuation could happen within a reasonable time frame [43]. The software was used by Akins et al. to study the natural attenuation of an underground fuel spill site in Oklahoma [44]. Bioscreen is generally set for describing the natural attenuation of BTEX compounds. It can be used for other chemicals, but the input data of the software needs to be adjusted according to the characteristics of the chemical [42].

In 2016, DTU Environment in collaboration with the Danish Minestry of Environment developed a a preliminary risk assessment tool named GrundRisk. By taking into account the typical contaminant transport mechanisms and processes of contaminated sites, the pollutants' concentrations can be simulated according to the source and the characteristics of the saturated and unsaturated zone. As a result, it is possible to estimate the fate of the chemicals in groundwater and to understand if they represent a risk for the groundwater quality.

2.3 Processes and factors determining the distribution of chemicals in the soil

A typical process happening between the soil and a chemical is defined as sorption. When the contaminants enters a soil, the contact between the contaminants and the soil brings to a reduction of the pollutant's velocity in the transport media [45]. The term is normally used to connect the phenomena of adsorption, i.e. the excess of the chemical's concentrations at the top of the soil, to the absorption of the chemical to the soil [46]. The distribution coefficient K_d [L^3/M] is an important parameter for estimating the adsorption of dissolved contaminants in a soil. It expresses the partitioning of the contaminant between the aqueous and the solid phase [47]. The value of K_d depends on the contaminant and the chemical properties of the two phases. When dealing with the sorption for organic pollutants (e.g. polycyclic aromatic hydrocarbons), the sorption in soil organic matter is assumed to be more dominant than the one to the mineral surfaces [48]. Equation 2.1 represents one of the most common approaches used for calculating the K_d [45]:

$$K_d = K_{oc} \times f_{oc} \tag{2.1}$$

The f_{oc} [-] is the weight fraction of organic carbon in the soil. A high f_{oc} means that the adsorption of the organic compounds to the aquifer is high. The K_{oc} [L^3/M] is the organic carbon/water partition coefficient. It is expressed as the ratio between the concentration in the organic carbon phase and the concentration in the water phase. A high value means a great link between the contaminants and the organic fraction of the soil. Because of its wide ranges, normally K_{oc} is expressed as $\log(K_{oc})$. This parameter is used to classify the contaminants' mobility, whose ranges are showed in Table 2.1. The higher is the $\log(K_{oc})$, the lower is the mobility [49].

Table 2.1: Classification of mobility of a chemical based on $\log(K_{oc})$ [49]

$\log(K_{oc})$	Classification
< 1	Highly mobile
1 - 2	Mobile
2 - 3	Moderately mobile
3 - 4	Slightly mobile
4 - 5	Hardly mobile
> 5	Immobile

Between the empirical relationships that have been developed to estimate the K_{oc}, the one with the K_{ow}, i.e. the octanol water partition coefficient, is the most commonly used [46]. The parameter indicates the ratio between a chemical's concentration in the octanol phase and its concentration in the aqueous phase. A high K_{ow}, i.e. above 10^4, indicates hydrophobic chemicals, while low K_{ow}, i.e. less than 10, indicates hydrophilic chemicals [50]. Normally, the Abdul's expression, which is obtained by the pollutants with $\log(K_{ow})$ values < 5 (i.e. non-hydrophobic) and soils with foc $< 0.1\%$, is one of the most common used [51]:

$$log(K_{oc}) = 1.04 \times log(K_{ow}) - 0.84 \tag{2.2}$$

If Equation 2.1 is combined with Equation 2.2, it is possible to calculate the distribution coefficient [45]:

$$log(K_d) = 1.04 \times log(K_{ow}) + log(f_{oc}) - 0.84 \tag{2.3}$$

The distribution coefficient of organic acids (e.g. chlorophenols) is calculated differently because these compounds are completely (or partially) ionized under normal pH values. Sorption depends on the charge of the ionization (+ or -), with repulsion occurring when the charges between the chemicals and the soils are the same [52]. The pollutants are strongly sorbed to the particle of soil when the charges are opposite. The more they are ionized, the stronger is the sorption [53]. Generally, the ionization of an organic acid "A" and the hydrogen "H" is described by Equation 2.4:

$$AH \leftrightarrow A^- + H^+, K_a = \frac{[A^-][H^+]}{[AH]} \tag{2.4}$$

K_a is the dissociation constant. K_a is often expressed by the acidity constant pK_a, which is equal to - $\log(K_a)$. The larger is the value of pK_a, the smaller is the dissociation [52]. The pH and pK_a values can be used in determining the neutral fraction ϕ_n [45]:

$$\phi_n = \frac{1}{1 + 10^{(pH - pK_a)}} \tag{2.5}$$

It is possible to estimate the K_d for organic acids through Equation 2.6 [45]:

$$K_d = f_{oc} \times (1.05 \times K_{ow}^{0.82} + 0.026 \times K_{ow}^{0.82} \times (1 - \phi_n)) \tag{2.6}$$

Equation 2.6 is only valid with $\log(K_{ow})$ values < 5 (i.e. hydrophilic) and soils with foc $< 0.001\%$. Otherwise, Equation 2.6 provides only a rough estimation of organic acids' sorption [45].

The factor used to describe the interactions between a chemical and a soil, which cause a delay of the chemical migration in the water, is called retardation factor R [-] [54]. It is normally calculated by Equation 2.7 [45]:

$$R = 1 + (\frac{K_d \times \rho_b}{n}) \tag{2.7}$$

The ρ_b [M/L^3] is the bulk density (i.e. the weight of soil in a given volume) and n [-] is the total porosity in the soil. If there is no sorption, the retardation factor is equal to one. As it can be seen, R is strictly dependent on the distribution coefficient K_d.

3. Study area

This chapter describes the principal physical and chemical characteristics of the contaminants revealed in the Pursiala aquifer. The area of Mikkeli has been always subjected to numerous industrial activities. As most of the Finnish aquifer, the one in Mikkeli is used by the local people for their domestic water needs. Consequently, an analysis on the aquifer's chemical conditions is necessary.

3.1 Characteristics of the area

Mikkeli has a population of 55000, and covers an area of almost 2125 km^2 [55]. Mikkeli has (generally) a cold and temperate temperature, with significant precipitation (about 634 mm/year), even during the driest months, and it is characterized by an average annual temperature of 3.7°C [55]. The Pursiala aquifer (see Figure 3.1) is located on an area of which 60% is constructed (e.g. roads, houses and pavements) and 10% is covered by water [23]. The area has a number of risks. The region has previously served for the rail traffic. In addition to that, potential chemicals, solvents and other substances, which are used by industries, can cause a high risk to the aquifer [23].

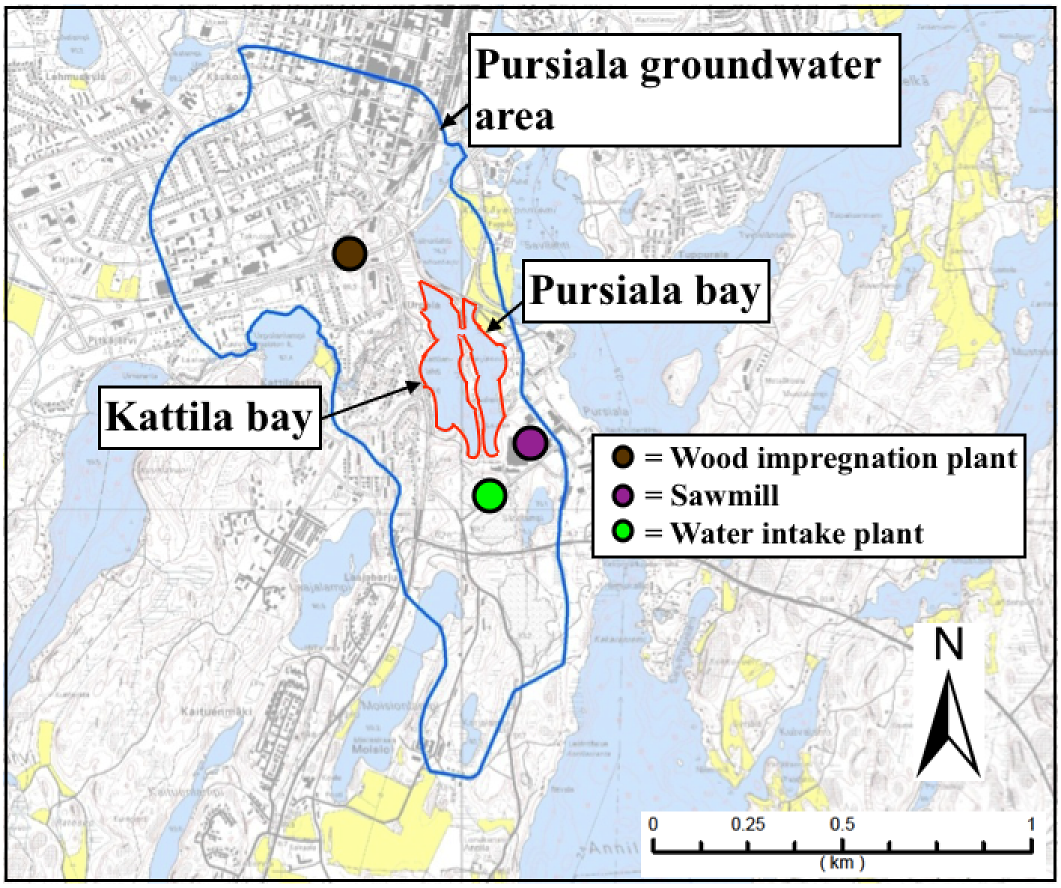


Figure 3.1: Areas studied [23]

The Pursiala groundwater area is classified as the most important resource for potable water in the city of Mikkeli [23]. The aquifer has an area of 4.3 km^2 and it is located in the southern part of the city [23]. The water intake is located on the ridge of the

Kattila and the Pursiala Bay, which are in the south part of the aquifer (see Figure 3.1). The ridge has a width of 700 m in the part located next to Mikkeli, of 500 m in the area of the two bays and of an average value between 200 and 300 m on the south part of the bays. The water yield is estimated to be of about 1700 m^3/day. [23]. In the north of the two bays, the ridge sinks below the the water level. Consequently, only some parts of the ridge are above the water table. The waters in the Kattila and the Pursiala Bay (see Figure 3.1) are in contact with each other because the ridge between the bays is not uniform but presents a narrow surface that assures a water connection [23].

As Figure 3.2 shows, the soil is composed of sand (and fine sand), gravel, silt and clay.

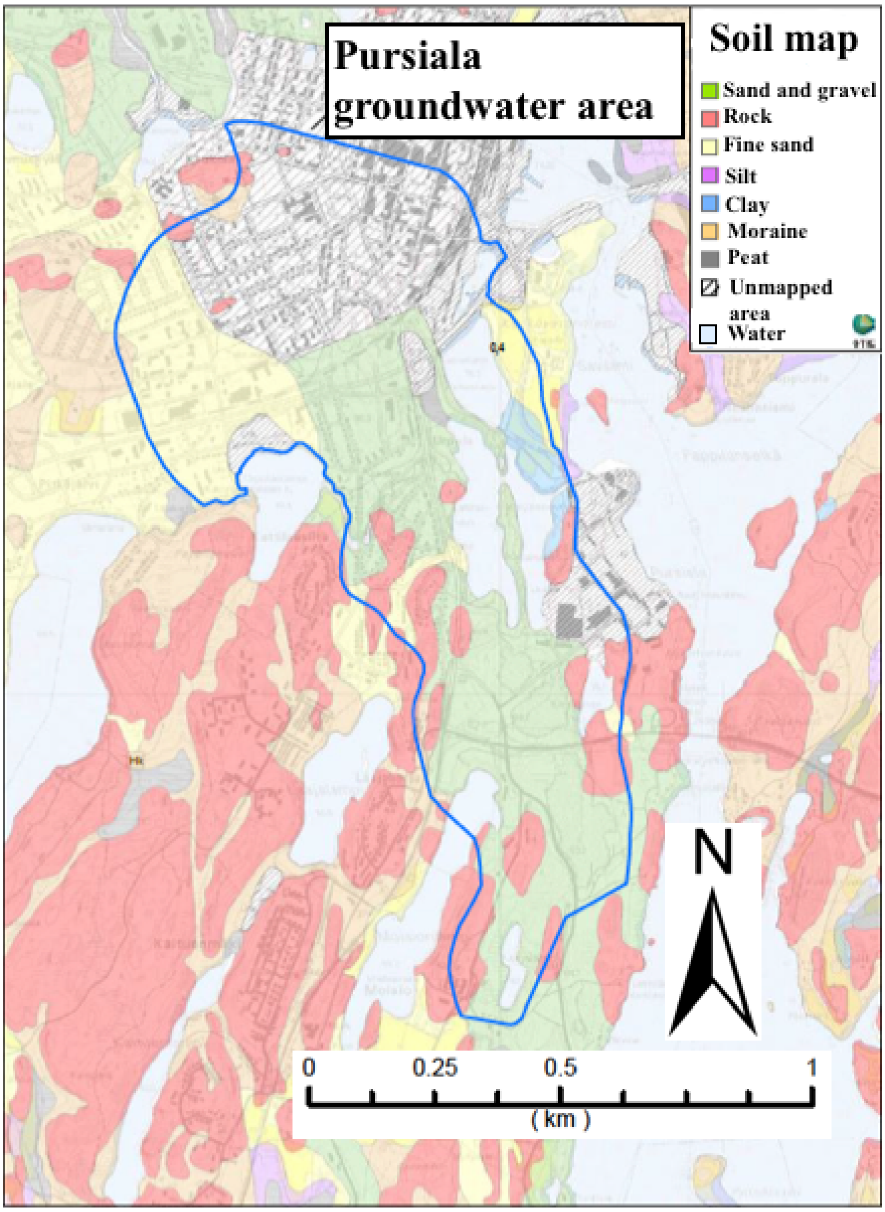


Figure 3.2: Soil map of Pursiala [23]

Figure 3.3 shows the the Pursiala area is characterized by wide areas of thin moraine and bedrock, in which (mostly) gneiss, quartz feldspar gneiss and granodiorite is present.

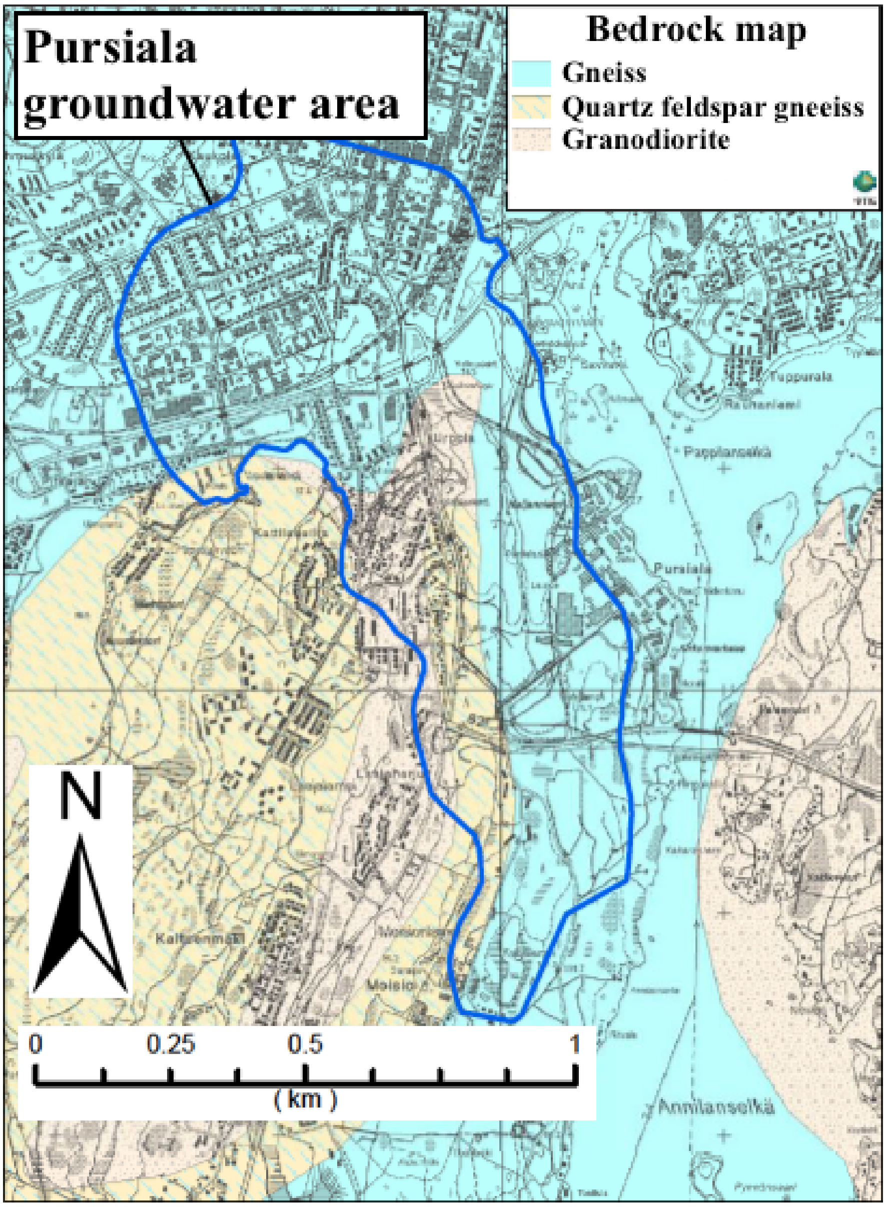


Figure 3.3: Bedrock map of Pursiala [23]

Due to the difficulties of obtaining sufficient information for conducting a detailed analysis on the groundwater area, it was decided to focus the work only on two locations (see Figure 3.1):

- a sawmill, which caused a contamination by chlorophenols. The area around it is of about 0.2 km^2;
- a wood impregnation plant. The activity caused a release of polycyclic aromatic hydrocarbons in the groundwater. The area around the plant is of about 0.1 km^2.

Table 3.1 lists the principal hydrogeological information of the areas around the sawmill and the wood impregnation plant. It is clear too see that the two areas present similar characteristics.

Table 3.1: Hydrogelogical characteristics of the areas of interest [56]

Parameter	**Sawmill area (CP contamination)**	**Wood impregnation plant area (PAH contamination)**
Aquifer media	Alluvium	Alluvium
Depth to water table [m]	5 - 10	10 - 15
Hydraulic conductivity [m/day]	30 - 50	60 - 80
Net recharge [mm]	250 - 300	280 - 330
Slope [%]	0 - 2	0 - 2
Soil media	Gravel-sand	Gravel
Vadose zone	Sand and gravel	Sand and gravel

The contaminated soil has been removed from the areas, i.e. it have been already remediated in several phases. The groundwater is still highly polluted by the above-mentioned contaminants, which are moving towards the water intake plant run by the city (see Figure 3.1). Therefore, remediation actions are still ongoing in Pursiala groundwater area.

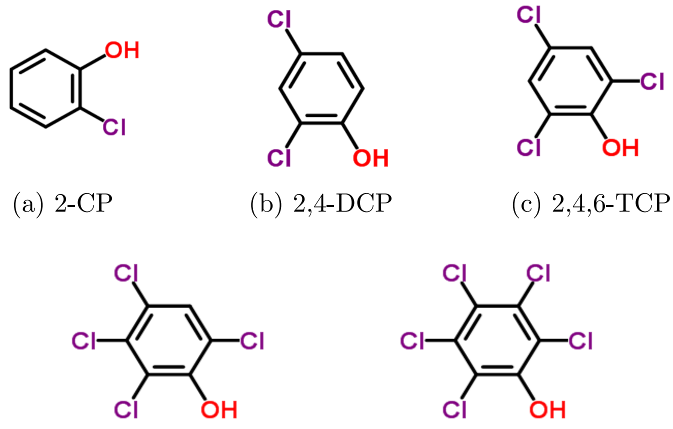
3.2 Chemicals of interest

This section describes the principal physical characteristics of the chemicals revealed in the two areas of interest, together with the groundwater guidelines, i.e. the maximum allowable concentration in groundwater that does not represent a threat for human health [57]. The groundwater guidelines were taken from the New Jersey Department of Environmental Protection, which estimated the maximum allowable concentrations in groundwater that guarantee safety of human beings [58].

3.2.1 Chlorophenols (CPs)

Chlorophenols (CPs) are the result of the addition of chlorines' atoms to phenol, which is derived from benzene through the replacement of a hydrogen by adding a hydroxy group to the carbon [59]. The CPs are produced in in chemical and pharmaceutical industrial activities or used as pesticides. They can enter the environment and most of them go into the water, with a small quantity in the air [59]. They can be present in drinking-water in different ways, such as the final result of the disinfection of phenols through chlorination, degradation products of phenoxy herbicides or as by-products of the reaction of hypochlorite with phenolic acids [60]. Five basic types of chlorophenols exist: monochlorophenols, dichlorophenols, trichlorophenols, tetrachlorophenols, and pentachlorophenols. Between all the 19 types of chlorinated phenols, 2-chlorophenols (2-CP, ClC_6H_4OH), 2,4-dichlorophenol (2,4-DCP, $Cl_2C_6H_3OH$) and 2,4,6-thrichlorophenol (2,4,6-TCP, $Cl_3C_6H_2OH$) are the compounds that are most likely to be found in drinking water [59]. Observation wells in the sawmill area at Pursiala reported the presence of 2,3,4,6-tetrachlorophenol (2,3,4,6-TeCP, $C_6H_2Cl_4O$)

and pentachlorophenol (PCP, C_6HCl_5O) in the aquifer. Their chemical structure is shown in Figure 3.4.



(a) 2-CP (b) 2,4-DCP (c) 2,4,6-TCP

(d) 2,3,4,6-TeCP (e) PCP

Figure 3.4: Chemical structure of Chlorophenols (CPs) [61]

The principal chemical and physical properties of chlorophenols are listed in Table 3.2. The densities are very similar in the 2,3,4,6-TeCP and the PCP, while it is lower in the first three chlorophenols. The Henry's law constants are similar in all the compounds, in exception of the one of 2-CP (it is higher). The vapor pressures are very different. Because all the compounds are solids in exception of 2-CP, which is liquid, no viscosity value was found for the other chlorophenols. In comparison to the other CPs, 2,4,6-TCP presents a very high solubility. On the other hand, the 2,3,4,6-TeCP is insoluble.

Table 3.2: Physico-chemical properties of Chlorophenols (CPs) [62]

Property	**2-CP**	**2,4-DCP**	**2,4,6-TCP**	**2,3,4,6-TeCP**	**PCP**
Density [g/cm^3]	1.2E+00	1.4E+00	1.5E+00	1.8E+00	1.9E+00
Vapor pressure [kPa]	2.0E-01 (at 20°C)	1.3E+02 (at 53°C)	1.3E+02 (at 76°C)	5.6E-04 (at 25°C)	1.3E-05 (at 25°C)
Viscosity [mPa$\times$s]	5.0E+00	-	-	-	-
Water solubility [μg/l at 25°C]	2.8E+04	4.5E+03	5.0E+05	-	1.4E+04
Henry's law constant [Pa m^3/mol]	1.2E+00	3.0E-01	4.0E-01	1.0E-01	3.0E-01

Table 3.3 gives an overview of the guideline values for the above-mentioned chlorophenols. The PCP is the compound with lowest groundwater guideline, i.e. it is the most harmful for human health, while 2,3,4,6-TCP has the highest guideline.

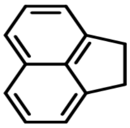
Table 3.3: Groundwater guidelines of Chlorophenols (CPs) [58]

Chemical	**2-CP**	**2,4-DCP**	**2,4,6-TCP**	**2,3,4,6-TeCP**	**PCP**
Groundwater guideline [μg/l]	40	20	1	200	0.3

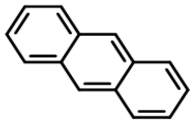
The connection between cancer risks and chlorophenols (CPs), especially on kidney and lungs was proved in several experiments [63]. Normally, by drinking water disinfected with chlorine, people can be exposed to little quantities of CPs because chlorination increases their concentrations in the water [59]. According to some studies, workers who produce pesticides from chlorophenols (and are therefore exposed to them through breathing and through the skin) develop acne and mild injury to their livers [59]. The dermal contact with chlorophenols causes a rapid penetration in the skin, which can be highly absorbed after oral administration [60]. Data in the Finnish city of Jarvela reported that the exposure to CP caused depression and asthma [64]. Experiments conducted by Wagner gave as result concentration of PCP found in kidneys [65]. There is no sufficient information about any birth defect of the chlorophenols: experiment on animals, in particular on rats, did not bring to any birth defect, but their exposure to high levels of chlorophenols showed a decrease in the weights of the newborns [59].

3.2.2 Polycyclic Aromatic Hydrocarbons (PAHs)

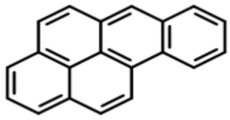
Polycyclic aromatic hydrocarbons represent a group of hydrocarbons that are mainly formed due to the incomplete degradation of organic materials (e.g. wood and oil), or represent emissions from anthropogenic activities (e.g. can be can be found in asphalt used in road construction) [66]. PAHs consist of three or more benzene rings containing only carbon and hydrogen. Every different configuration leads to diverse properties [67]. PAHs are not found in water at very high concentrations because of their high affinity for particulate matter and their low solubility [68]. Generally there are more than 100 species of PAHs and they occur as mixtures. They are colorless and can have a pleasant odor [66]. As mentioned before, the wood impregnation plant brought to a release of a series of polycyclic aromatic hydrocarbons. In particular, the source area consists of acenapthene ($C_{12}H_{10}$), anthracene ($C_{14}H_{10}$), benzo(a)pyrene ($C_{20}H_{10}$ and it is the most studied PAH [68]), chrysene ($C_{18}H_{12}$), fluoranthene ($C_{16}H_{10}$), fluorene ($C_{13}H_{10}$), napththalene ($C_{10}H_8$), phenanthrene ($C_{14}H_{10}$) and pyrene ($C_{16}H_{10}$). Their chemical structure is shown in Figure 3.5.



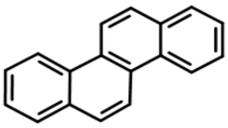
(a) Acenaphthene



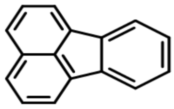
(b) Anthracene



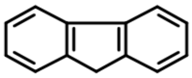
(c) Benzo(a)pyrene



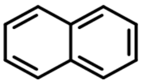
(d) Chrysene



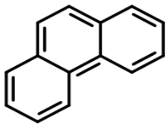
(e) Fluoranthene



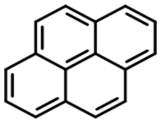
(f) Fluorene



(g) Naphthalene



(h) Phenanthrene



(i) Pyrene

Figure 3.5: Chemical structure of Polycylic Aromatic Hydrocarbons (PAHs) [61]

Table 3.4 and 3.5 list the principal physical and chemical characteristics for the PAHs described above. As it can be seen, most of the these compounds are basically insoluble in water and are characterized by a very low vapor pressures and viscosity. In addition, the density of these chemicals is very similar and they present a very low volatility [69].

Table 3.4: Physico-chemical properties of Polycyclic Aromatic Hydrocarbons (PAHs) - first part [62, 68]

Property	**Acenaphthene**	**Anthracene**	**Benzo(a)pyrene**	**Chrysene**	**Fluoranthene**
Density [g/cm^3]	1.1E+00	1.3E+00	1.2E+00	1.3E+00	1.2E+00
Vapor pressure [kPa at 25°C]	2.9E-04	1.0E-06	7.3E-05	8.3E-11	1.2E-06
Viscosity [mPa×s]	-	4.0E-01 (at 300°C)	-	-	6.0E-01 (at 20°C)
Water solubility [μg/l at 25°C]	3.9E+03	4.4E+01	3.8E+00	2.0E+02	2.6E+02
Henry's law constant [Pa m^3/mol]	1.8E+01	4.6E+00	4.6E-02	1.0E-01	9.0E-01

Table 3.5: Physical properties of Polycyclic Aromatic Hydrocarbons (PAHs) - second part [62, 68]

Property	Fluorene	Naphthalene	Phenanthrene	Pyrene
Density [g/cm^3]	1.2E+00	1.2E+00	1.2E+00	1.3E+00
Vapor pressure [kPa at 25°C]	8.0E-06	1.1E-02	1.6E-05	6.0E-07
Viscosity [mPa$\times$s]	-	7.0E-01	-	-
Water solubility [μg/l at 25°C]	1.7E+02	3.1E+04	1.6E+03	1.3E+02
Henry's law constant [Pa m^3/mol]	9.7E+00	4.5E+01	4.2E+00	1.9E+00

The PAH groundwater guidelines are shown in Table 3.6 and 3.7. Benzo(a)pyrene is the one with the lowest guideline value, while anthracene is the chemical with the highest guideline. Consequently, they are, respectively, the most and the least harmful for human beings.

Table 3.6: Groundwater guidelines of Polycyclic Aromatic Hydrocarbons (PAHs) - first part [58]

Chemical	Acenaphthene	Anthracene	Benzo(a)pyrene	Chrysene	Fluoranthene
Groundwater guideline [μg/l]	400	2000	0.005	5	300

Table 3.7: Groundwater guidelines of Polycyclic Aromatic Hydrocarbons (PAHs) - second part [58]

Chemical	Fluorene	Naphthalene	Phenanthrene	Pyrene
Groundwater guideline[μg/l]	300	300	100	200

It is known that cancer risk is associated to the exposure of polycyclic aromatic hydrocarbons (PAHs), but unfortunately necessary data regarding human risks due to oral exposure are missing [66]. People are exposed to PAHs in many different ways, e.g. by breathing due to the attachment of these chemicals to the dust and to other particles in the air [70]. Numerous experiments on animals stated that most PAHs leave the body within a few days through urine and feces [66]. The sources of PAHs can vary from the cigarette smoke and to the industrial activities (e.g. production of petrochemicals) [71]. In particular, PAHs can be present in smokes from wood fires or tobacco smoke. The inhalation of cigarette/wood smoke or air containing these compounds can cause damage to the breathing and the lungs [72]. In addition, the contact of soil containing high quantities of PAHs easily allows the access of these chemicals in the body, with the quantity strictly related to the presence of other compounds when exposed to PAHs [66]. Several studies revealed that people exposed for a very long period to

PAHs by breathing or by skin contact may develop cancer [71]. This is also proved by the experiments on animals, which have developed tumors after being exposed to PAHs by either breathing or skin contact [66].

3.3 Risk management actions

The goal of this section is to (briefly) describe the remediation technologies (physico-chemical and biological) that are nowadays applied to reduce the CP and PAH concentrations in the two areas of the Pursiala aquifer.

3.3.1 Sawmill area

The sawmill area has been subjected to a series of biological remediation processes (i.e. bioremediation). Chlorophenols (CPs) have been transformed aerobically (oxidative dechlorination) by adding oxygen to water. Normally, the oxygen is inserted in pure form by avoiding the contact between atmospheric air and groundwater. In this way it is possible to insert high quantity of oxygen (something that does not happen when it is in dissolved form) [73]. The bioremediation has some limitations because this procedure must be tailored to the site-specific conditions. In other words, treatability studies must be executed on a small scale before the actual clean-up of the sites [74]. On the other hand, the technique is very efficient for the treatment of dissolved and sorbed contaminants [75] because it can increase the rate of dissolution and desorption of contaminants [76]

Because the addition of oxygen to anoxic groundwater did not always result in increased aerobic biodegradation, the oxidation was improved by adding, though groundwater wells, calcium peroxide (CaO_2), i.e. an oxidant that, by definition, has the ability to oxidize other substances by removing electrons from another substance. As a consequence, the oxidant becomes reduced itself. This operation is called In Situ Chemical Oxidation or ISCO (in situ because it is conducted in place). As Figure 3.6 shows, once the oxidants are injected, they spread in the soil and groundwater and react with the contaminants [77]. It is difficult to indicate the costs of the ISCO method. Generally, they depend on the quantity of the injected oxidant, which is related to the contaminants' oxidant demand, the natural oxidant demand NOD (i.e. the oxidant naturally consumed by the organic and inorganic species) and the oxidant persistence in the subsurface [78]. The NOD is a key parameter that affects the feasibility of the ISCO, and it is complex to determine due to its correlation to the mass of oxidant [79]. Nevertheless, it is a very efficient technique because it guarantees large reductions of concentration and mass flux within a short time frame [78].

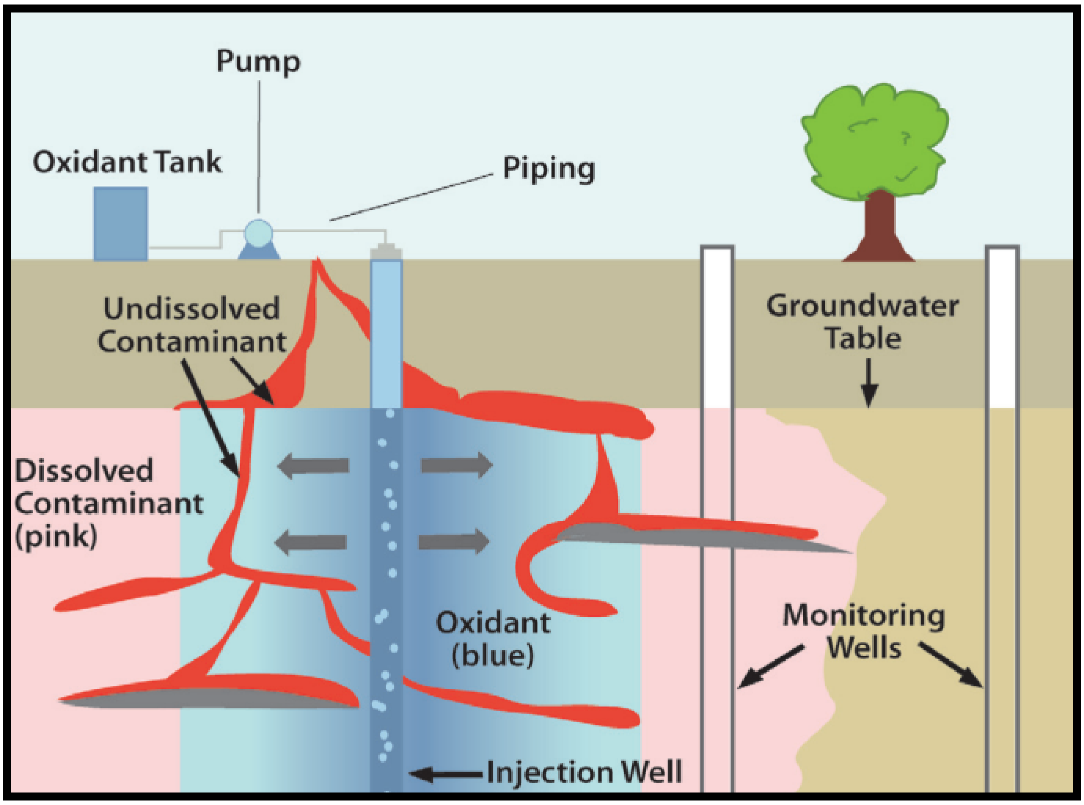


Figure 3.6: In Situ Chemical Oxidation [77]

3.3.2 Wood impregnation plant area

In the area around the wood impregnation plant, the concentrations of polycyclic aromatic hydrocarbons (PAHs) have been reduced through the application of a pump and treat system. No information may be collected about the specific PAH treatment in this area. Generally, the concept of a pump and treat system is very simple: contaminated groundwater is extracted, treated and then discharged to a sewer [80]. The extracted water is replaced with clean water. To be precise, the water is pumped out by using a vacuum pump. The contaminants are purified through a series of vessels, which contains particular materials designed to adsorb the contaminants themselves [81]. Normally, the efficiency of the system can be improved by using sand filters or chemical reagents such as flocculants [82].

Figure 3.7 describes in details the design of the system. It is normally characterized by one (sometimes more) well equipped with pumps. The groundwater is pulled out into the wells and up to the surface where the water, after being moved from a holding tank to a treatment system, is cleaned [83]. During its applications, contaminants keep on dissolving. As a consequence, the time frames for acceptable clean-up might become too long [80]. The efficiency of the pump and treat system can vary according to the soil type and the geology [81]. In addition, the sorption can influence the time of remediation: when dealing with a site with sorbed contaminants, the cleanup times depend on the desorption time of the contaminants, which is related to the organic carbon and the solubility of contaminants [84].

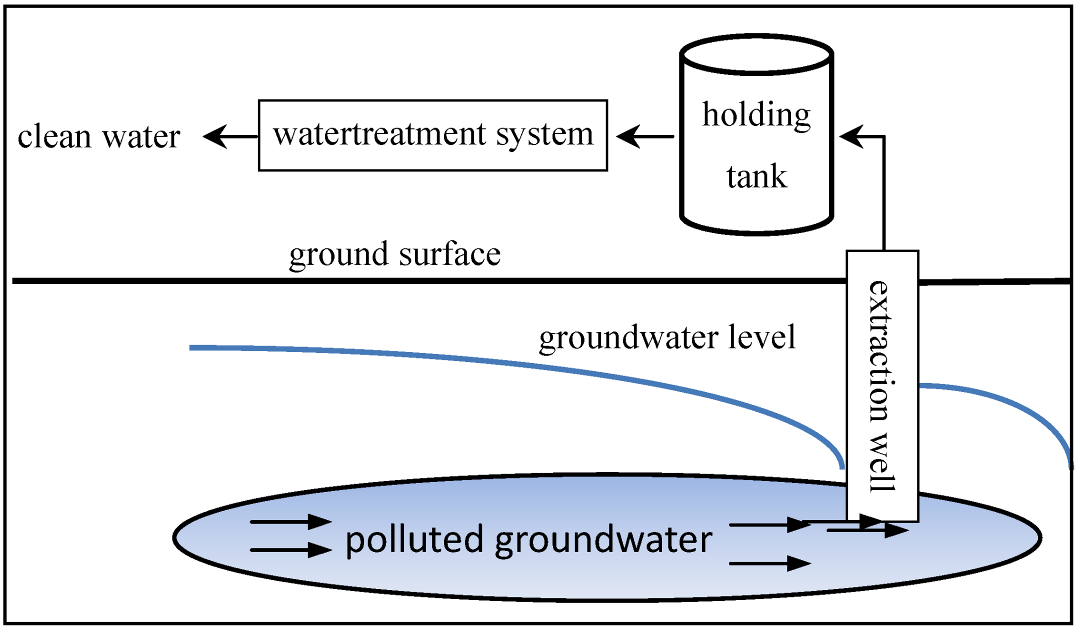


Figure 3.7: Typical pump and treat system [83]

4. Materials and methods

This chapter presents the methods used in the Master's Thesis. The the vulnerability of the aquifer was determined with the DRASTIC method, which is the most common method used in Finland (see Chapter 4.3). The dispersion of the contaminants in the Pursiala aquifer was modelled by using GrundRisk (see Chapter 4.4). It was chosen between all the other tools because it is a new software and it is still in development in Denmark. In addition to that, considering that the Master's project is in collaboration with the Technical University of Denmark, it may be interesting to investigate the applicability of the tool to Finnish conditions. Lastly, the human health risk assessment was conducted to describe the exposure routes and the doses through which the people of Mikkeli might be exposed (see Chapter 4.5).

4.1 Concentration data on the contaminants in the Pursiala aquifer

The concentrations of the contaminants in the Pursiala aquifer were obtained from the Finnish national groundwater database POVET, which officially started in 2002. The database contains all the detailed information about the aquifer (e.g. land use and hydrogeology), as well as information about groundwater sampling from ponds and wells [85]. The information collected from those wells covers a period of 40 years, from 1976 to 2016, with 89524 field measurements. For the purpose of the Master's Thesis, the analysis was focused only on the groups of CPs and PAHs.

The concentrations are listed in the database according to the well, the time of measurement and the depth. For each chemical, the maximum concentration was taken into account, together with the mean value, the standard deviation STDEV. It is the value that expresses how much the data of a group differ from the mean value of the group itself. A higher standard deviation indicates a high dispersion in the data. The 95% upper confidence limit UCL was calculated by Equation 4.1:

$$UCL = mean + 2 \times STDEV \tag{4.1}$$

The concentrations of the POVET database were compared to the groundwater guidelines. As it can be seen from Table 4.1, chlorophenols have the highest concentrations measured, with all of the compounds exceeding the groundwater guideline. Between the PAHs, acenaphthene, benzo(a)pyrene, naphthalene and pyrene execeed the guidelines. The chemical condition of the aquifer became clearer with these results and the chemicals of potential concern, i.e. the ones above the groundwater guideline and that are most likely to have a health effects on human beings, were identified. In addition, this analysis proved that the remediation technologies applied in the Pursiala area are insufficient. Therefore, the state of the groundwater and risks need to be assessed in more detail.

Table 4.1: Concentrations of Chlorophenols (CPs) and Polycyclic Aromatic Hydrocarbons (PAHs) detected in the POVET wells installed in the Pursiala aquifer. The value is highlighted in blue if it is above the groundwater guideline [86]

Chemical	**Unit**	**Groundwater guideline**	**Max**	**Mean**	**STDEV**	**95% UCL**
2-CP	μg/l	40	6.6E+02	7.0E-01	4.5E+00	9.7E+00
2,4-DCP	μg/l	20	9.0E+02	3.5E+02	4.8E+02	1.3E+04
2,4,6-TCP	μg/l	1	5.0E+04	1.8E+04	1.5E+04	4.8E+04
2,3,4,6-TeCP	μg/l	200	4.9E+04	9.3E+02	1.1E+04	3.1E+04
PCP	μg/l	0.3	4.7E+04	1.2E+04	1.3E+04	4.0E+04

Chemical	**Unit**	**Groundwater guideline**	**Max**	**Mean**	**STDEV**	**95% UCL**
Acenaphthene	μg/l	400	4.7E+02	6.8E+01	9.4E+01	2.6E+02
Anthracene	μg/l	2000	9.1E+00	1.8E+00	1.8E+00	5.9E+00
Benzo(a)pyrene	μg/l	0.005	1.5E+00	6.0E-01	5.0E-01	1.6E+00
Chrysene	μg/l	5	2.8E+00	8.0E-01	8.0E-01	3.9E+00
Fluoranthene	μg/l	300	3.7E+01	4.1E+00	7.2E+00	1.1E+02
Fluorene	μg/l	300	1.5E+02	3.3E+01	3.7E+01	1.6E+02
Naphthalene	μg/l	300	9.7E+02	5.5E+01	1.6E+02	3.5E+02
Phenanthrene	μg/l	100	1.4E+02	2.6E+01	3.0E+01	8.7E+01
Pyrene	μg/l	200	1.9E+01	2.1E+00	3.8E+00	9.8E+00

4.2 Concentrations of contaminants in the areas of interest

The source area was measured over a time period of 9 years (2004-2013). The maximum measured soluble PAH-compound concentration was taken into account in the analysis. 9 PAH compounds were detected in the source area (see Chapter 3.2.2). The groundwater risk assessment was based on them. The concentrations were provided by the company WaterHope. Table 4.2 shows the PAH concentrations measured in the source area in the aquifer. Phenanthrene is the contaminant with the highest concentration measured, while benzo(a)pyrene with the lowest one.

Table 4.2: Concentrations detected in the source area, in the Pursiala aquifer, of Polycyclic Aromatic Hydrocarbons (PAHs) around the wood impregnation plant [56]

Chemical	**Concentration [μg/l]**
Acenaphthene	1460
Anthracene	180
Benzo(a)pyrene	54
Chrysene	171
Fluoranthene	823
Fluorene	1050
Naphthalene	813
Phenanthrene	1640
Pyrene	584

The concentrations in the groundwater area around the sawmill were compiled between 2015 and 2017 in wells installed by the Finnish Consulting Group (FCG). Figure 4.1 shows the location of the wells. The pumping wells, which were installed in the area, may bring to a drastic change of the groundwater level in the area.

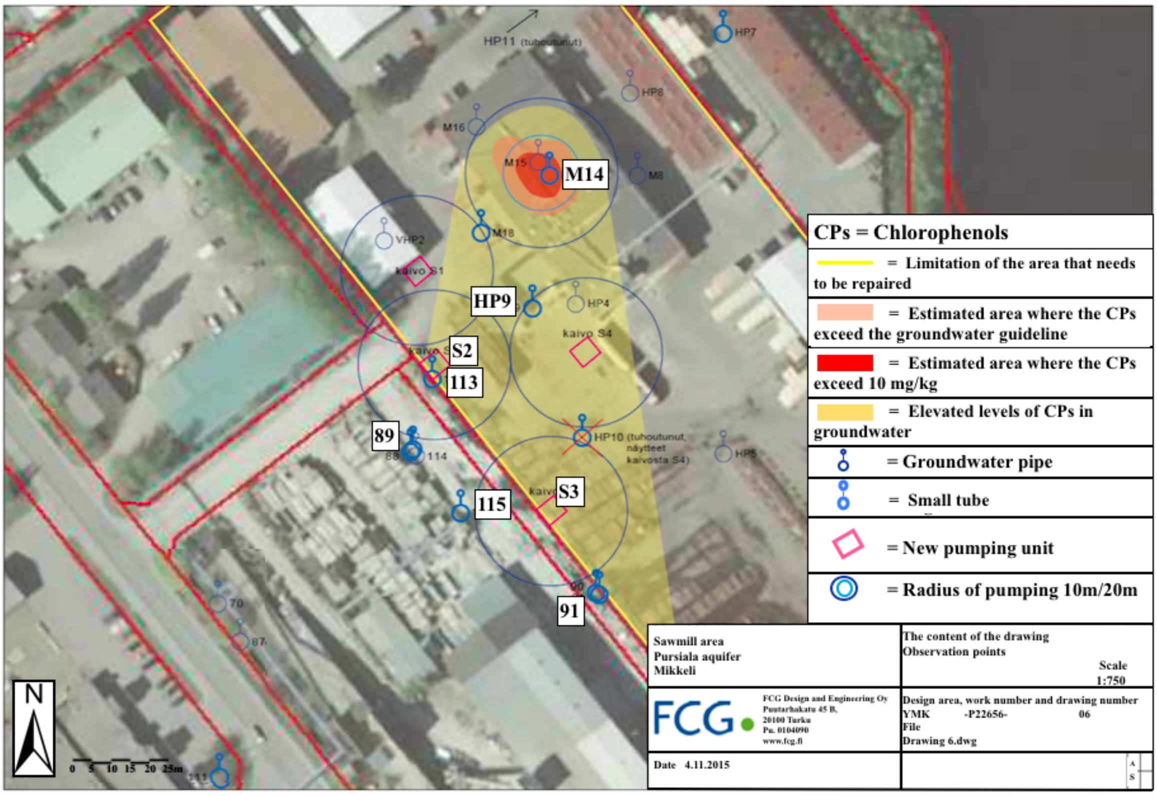


Figure 4.1: Wells installed by the Finnish Consulting Group (FCG) between 2015 and 2017. The wells considered for the analysis are highlighted [87]

Table 4.3 summarizes the concentrations detected in 156 samples of these well. More detailed information regarding these concentrations can be found in Table 1 and 2 in Appendix 1. Some of the wells were excluded from Table 1 because the concentrations detected in those wells were very low. It was therefore decided to focus the analysis only on those wells whose concentrations were more relevant. The FCG wells considered in the study are highlighted in Figure 4.1. The maximum of 2-CP was found in well S3, of 2,4-DCP in well 91, of 2,4,6-TCP in well 115 and 2,3,4,6-TeCP and PCP in well M14, i.e. where the source is located (see Figure 4.1 and Table 1 in Appendix 1).

Figure 4.2 shows a comparison between the concentrations in the Pursiala aquifer compiled in POVET and by the Finnish Consulting Group. Some differences can be drawn. The 2-CP, 2,3,4,6-TeCP concentrations in the POVET database are lower than the ones sampled by the FCG, while the ones of 2,4-DCP, 2,4,6-TCP and PCP are higher.

Table 4.3: Concentrations of Chlorophenols (CPs) detected in 156 samples of the wells installed by the Finnish Consulting Group (FCG) in the Pursiala aquifer. The value is highlighted in blue if it is above the groundwater guideline [87]

Chemical	Unit	Groundwater guideline	Max	Min	Mean	STDV	95% UCL
2-CP	μg/l	40	3.9E+02	0	4.4E+00	3.1E+01	6.6E+01
2,4-DCP	μg/l	20	2.9E+02	0	3.3E+01	5.0E+01	1.3E+02
2,4,6-TCP	μg/l	1	3.1E+03	0	3.2E+02	5.3E+02	1.4E+04
2,3,4,6-TeCP	μg/l	200	1.0E+05	1.0E-01	4.6E+04	9.9E+04	2.5E+05
PCP	μg/l	0.3	2.4E+03	0	2.2E+02	3.1E+02	8.5E+02

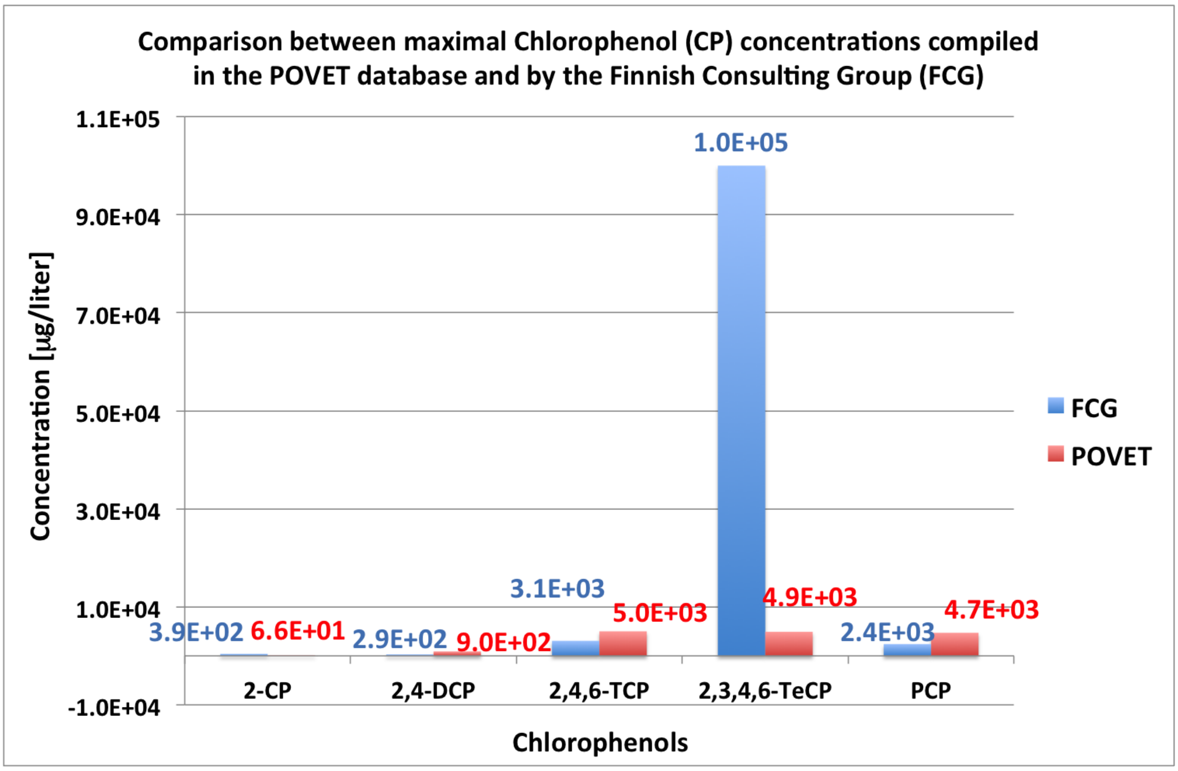


Figure 4.2: Comparison between maximum Chlorophenol (CP) concentrations detected by the POVET database and the Finnish Consulting Group (FCG) (the value is colored if it is above the groundwater guideline)

The human health risk assessment was executed only on the concentrations compiled by FCG. The decision was drawn by two factors. Firstly, the results from the POVET database (see Table 4.1) were estimated considering the whole aquifer, while the ones from FCG (see Table 4.3) are specifically on the sawmill area (i.e. the area of interest). Secondly, the samples from FCG are more recent than the ones from POVET, and they were therefore assumed more reliable.

4.3 Vulnerability analysis

DRASTIC [30] is a method that is used worldwide thanks to the accurate results that are obtained, despite the complex hydrogeological structure of the aquifers [34]. DRASTIC is an acronym for:

- **D**, i.e. the depth from the ground surface to the water table, in an unconfined aquifer, or to the bottom of the confining layer, in a confined aquifer. It tells the distance that needs to be traveled by the contaminant to reach the water table [88];
- **R**, i.e. the net recharge. It is the total quantity of water applied to the ground surface, which infiltrates to reach the aquifer. It is important because, due to the infiltration, the contaminant moves with the rainfall and goes into the saturated layer of the aquifer [33];
- **A**, i.e. the aquifer soil type. The parameter has information on the geological formation of the area [33];
- **S**, i.e. the soil type layer, which extends only to few meters from the surface. It represents the portion of the vadose zone with a significant biological activity. The impact is especially high on the recharge water's movement, which infiltrates into the aquifer and affects the downward movement of the contaminants into the vadose zone [89];
- **T**, i.e. the topography or the slope of the land surface. Hilly terrains have a higher slope in comparison to flat ones. The runoff is higher and the time of water contact and infiltration is lower. This means that hilly terrains are less vulnerable than flat terrains [33];
- **I**, i.e. the impact of the type of soil of the vadose zone. It is the area above the water table and it can be unsaturated or discontinuously saturated [33];
- **C**, i.e. the hydraulic conductivity. It tells the ease of the water to flow in the saturated zone. Through this parameter, it is possible to check the contaminant's transportation [33].

Through a linear combination of these seven hydrogeological parameters, as Figure 4.3 shows, DRASTIC can estimate the vulnerability of the aquifer. As a result, a fair preliminary analysis, for identifying vulnerable areas and understanding policy, decision making and management plans, is obtained [33]. Generally, DRASTIC is integrated together with GIS tools (e.g. ArcGIS) in order to have maps for groundwater according to each parameter. Due to the lack of geo-referential data in the Finnish databases, it was not possible to draw GIS maps.

The so-called DRASTIC vulnerability index (DVI) is calculated to determine the vulnerability of the aquifer. The higher the DVI is, the more vulnerable the aquifer is. The index is determined from Equation 4.2:

$$\begin{aligned} DVI = {} & D_r \times D_w + R_r \times R_w + A_r \times A_w + S_r \times S_w + T_r \times T_w \\ & + I_r \times I_w + C_r \times C_w \end{aligned} \tag{4.2}$$

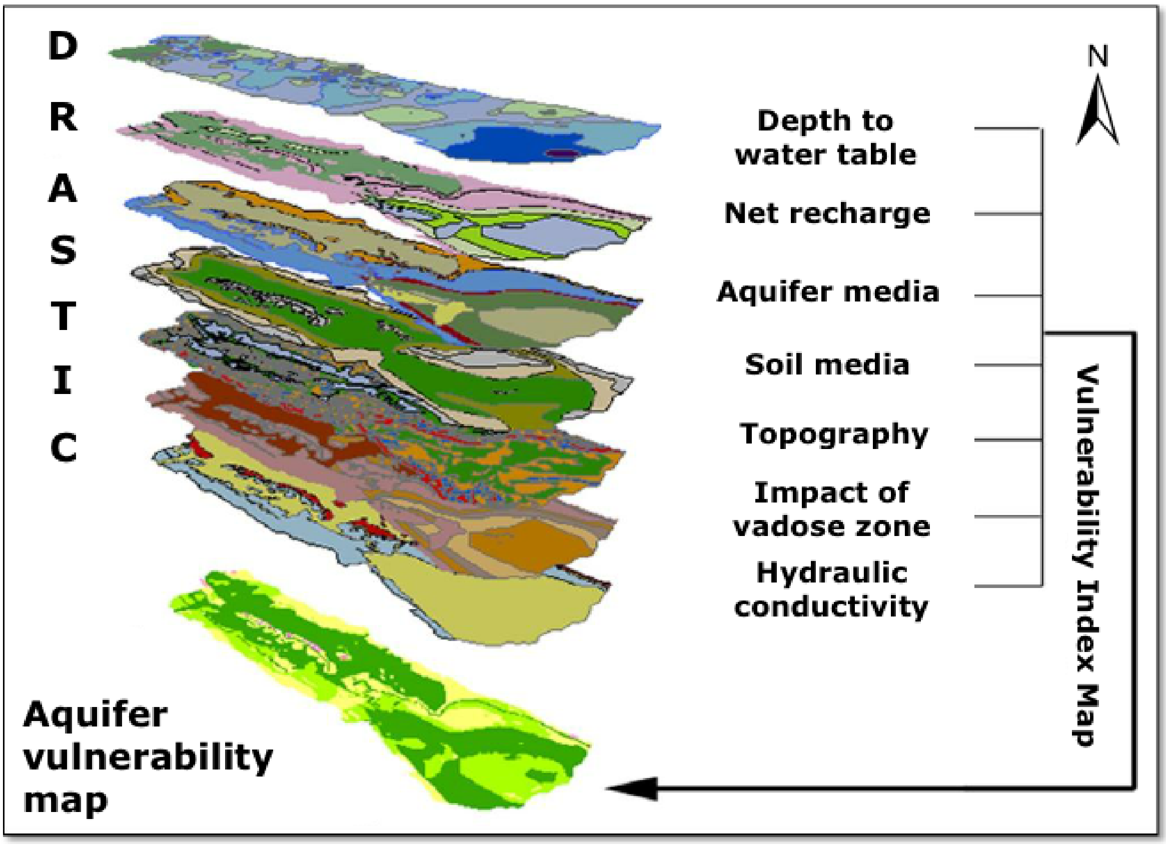


Figure 4.3: Visualization of the seven DRASTIC parameters [90]

The index r and w indicate the rating and the weight assigned to the parameter: for r, the scale ranges from 1 to 10, in which 1 denotes the least vulnerable while 10 is the most vulnerable areas; for w the scale is from 1 to 5, where 1 is the least significant parameter and 5 is the most. The rating's ranges are calculated according to the area. The knowledge of the hydrogeology and geology of the site is therefore fundamental [33]. The ratings and the weights of the parameters, provided by the environmental protection agency US EPA, are described in detail in Table 4.4. According to these values, the DVI goes from 31 to 226, which indicates, respectively, a low and high vulnerability.

The DRASTIC method is very advantageous. DRASTIC is able to limit the errors that might arise due to factors such as the uncertain value of the parameters or the influence of the parameters on the DVI value [91]. In order to obtain a further knowledge on the parameters and on the role they play in the vulnerability of the aquifer, a sensitivity analysis can be conducted [34]. It is possible to identify two types of sensitivity analysis:

- the map removal sensitivity, which was elaborated by Lodwick et al. [35]. The DVI sensitivity is determined through the removal of one or more parameters. It is calculated by Equation 4.3:

$$SI = \frac{\left|\frac{DVI}{N_p} - \frac{DVI'}{N'_p}\right|}{DVI} \times 100 \tag{4.3}$$

Table 4.4: Range, rating, weight and total weight of the DRASTIC parameters [88] [30]

Parameter	Parameter range	Parameter rating	Parameter weight	Parameter total weight
D: Depth to water table [m]	0 - 2.5	10	5	50
	2.5 - 4	7		35
	4 - 6.5	5		25
	6.5 - 9	3		15
	$9 \geq 12.5$	1		5
R: Net recharge [mm]	0 - 50.80	1	4	4
	50.80 - 101.60	3		12
	101.60 - 177.80	6		24
	177.80 - 254	8		32
	> 254	9		36
A: Aquifer media [-]	Alluvium	10	3	30
	Limestone	9		27
	Conglomerate	8		24
	Volcanic	7		21
	Flysch	3		9
S: Soil media [-]	Absent	10	2	20
	Gravel-sand	9		18
	Gravel	8		16
	Sandy clay	3		6
	Clay loam	2		4
T: Topography or slope [%]	$0 < 2$	10	1	10
	$2 < 6$	9		9
	$6 < 12$	5		5
	12 - 18	3		3
	> 18	1		1
I: Impact of vadose zone [-]	Limestone	10	5	50
	Basalt	9		45
	Sand and gravel	8		40
	Sandstone	6		30
	Tuff	3		15
	Clay	1		5
C: Hydraulic conductivity [m/day]	0 - 29.005	1	3	3
	29.005 - 72.7	3		9
	72.7 - 116.4	5		15
	116.4 - 160.1	7		21
	160.1 - 203.79	9		27
	203.79 - 247.84	10		30

SI [%] is the sensitivity index, DVI and DVI′ are the indexes obtained, respectively, with all the parameters and by excluding one or more parameters, and N_p & N'_p are the number of parameters used for calculating the indexes. When more than one parameter is removed, the parameters are excluded in ascending order. The removal proceeded by firstly eliminating the parameters which play less variation on DVI and so on;

- the single parameter sensitivity, which was used for the first time by Napolitano and Fabbri [36], and that allows studying the impact of the parameters on the value of the DVI index. Equation 4.4 is used:

$$W = \frac{P_r \times P_w}{DVI} \times 100 \tag{4.4}$$

W [%] is the effective weight of a single parameter, P_r and P_w are the rating and the weight of the parameter (see Table 4.4). The effective weight can be seen as a function of the value of the single parameter with regard to the weight assigned to it by the DRASTIC model [24]. In a typical case study, W is firstly calculated from the theoretical DRASTIC values (see Table 4.4), and then from the DRASTIC values assigned in the case study. In this way, it is possible to calculate the effective parameter weight by using Equation 4.5:

$$(Parametertab : PAH Dermal exposure dose for males according to different hours weight)_{Theoretical} :$$
$$(Parameter\ weight)_{Effective} : (W)_{Effective} \rightarrow$$
$$(Parameter\ weight)_{Effective} = \frac{(Parameter\ weight)_{Theoretical} \times (W)_{Effective}}{(W)_{Theoretical}} \tag{4.5}$$

Despite the ease of the DRASTIC method, a large amount of monitoring and field investigations are required. Data on land use and cover can be used to assess the areas where water resources are under stress [33].

4.4 Modelling contaminants' transport

4.4.1 Principles of the GrundRisk model

GrundRisk was chosen to describe the dispersion of the contaminants in the aquifer. Figure 4.4 shows the conceptual model for the GrundRisk transport model. Five different models can be applied. All of them deal with a vertical and a horizontal transport. The former simulates the changes of contaminant concentrations (due to degradation and dispersive processes) between the source and the top of the groundwater aquifer, while the latter simulates the subsequent transport and resulting concentrations in the aquifer [92]. The models are based on the same assumptions [92]:

- the soil is homogeneous, i.e. the soil and contaminant parameters (e.g. bulk density and degradation rates) are constant in space and time;
- the sorption processes (see Chapter 2.3) between the water and solid phase are linear and reversible;
- the advection occurs at constant velocity and only in the water phase in one dimension;
- the first order kinetics describes the degradation and occurs only in the water phase (with the first order degradation rate λ);
- the contaminant mass discharge and the concentration in the contaminant source are constant in the time.

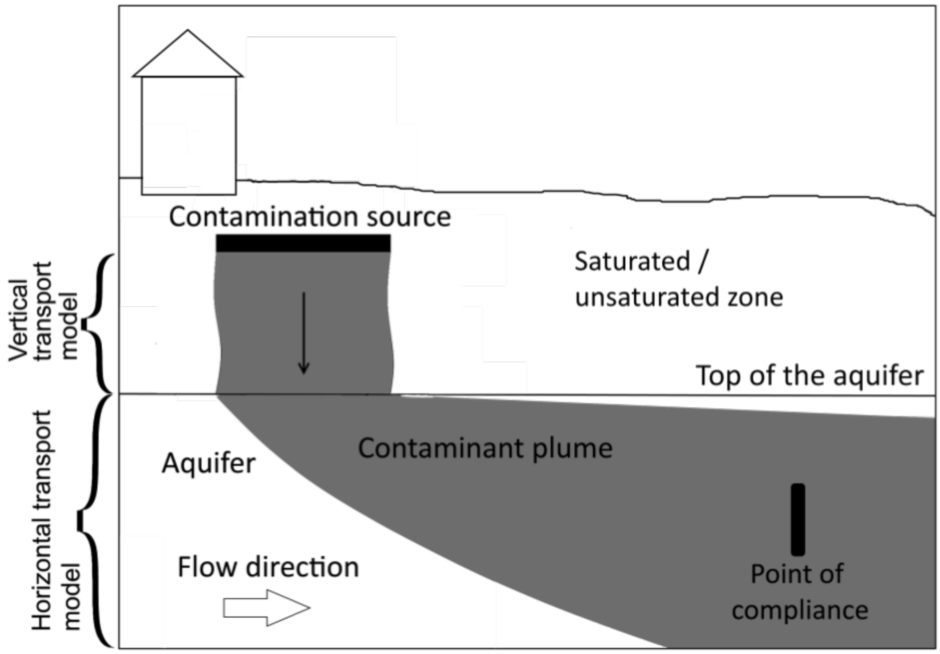


Figure 4.4: GrundRisk transport model [92]

The models are applied in Matlab and the code presents the same structure for all the contaminants. It is possible to obtain three different outputs: concentration downstream (x direction), across the downstream distance (y direction) and in the vertical distance at a point located from the downstream edge of the source area (z direction). The four remaining models are [92]:

- **Model I: Homogeneous saturated clay overlying an aquifer**. It simulates the concentrations in the water phase in a saturated clay between the contaminant source and an underlying aquifer with a 1D steady-state analytical solution; no dispersion is assumed in the solution. The model gives as an output the concentration at the top of the aquifer, which is simulated through an horizontal 3D steady state analytical solution (it includes both dispersion and advection);

- **Model II: Fractured saturated clay overlying an aquifer**. The water phase concentration in saturated fractured clay layers is simulated using a vertical 1D steady-state analytical solution which assumes advective transport in the fractures and diffusive transport in the matrix. The concentration in the aquifer is described with the same horizontal model described in Model I;

- **Model III: Unsaturated zone overlying an unconfined aquifer**. In this case, the vertical model simulates the concentration in the water phase, at the top of the aquifer, by using a 3D steady-state solution. As before, the result of the vertical model is the output of the horizontal model, which is calculated with a 3D model. In comparison to the previous ones, the model includes now the contaminant mass flux J;

- **Model IV: Unsaturated zone under an impervious area with zero infiltration**. The fourth model considers an unsaturated zone overlying the unconfined aquifer with no infiltration flux I. The concentration in the unsaturated zone is simulated using a 2D steady-state analytical, while the concentration in the aquifer is simulated through the same 3D model (with slight differences) used in model III;

- **Model V: Direct input from the contaminant source to the groundwater aquifer**. It only simulates the concentration in the aquifer by using a 3D horizontal model (the same used in Model I and II), with no vertical model because the concentration is already in the aquifer.

The contaminants are already in the aquifer. The most suitable model for the purpose of the Master's Thesis is Model number V. Its conceptual model is showed in Figure 4.5. The conceptual models of the other four models are showed in Figure 1 and 2 in Appendix 2.

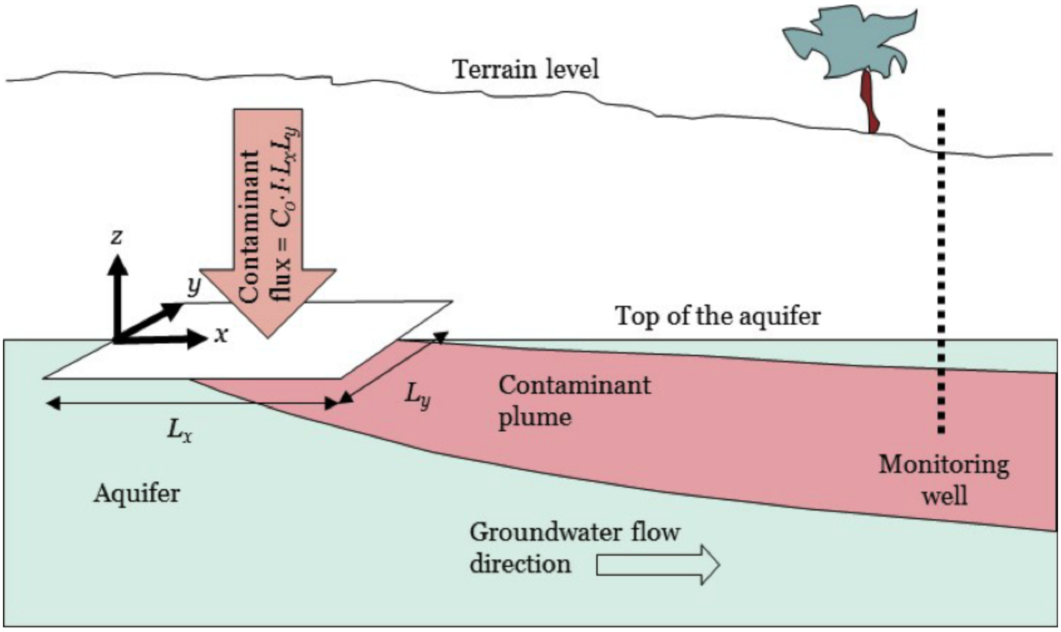


Figure 4.5: GrundRisk conceptual model number V applied in the study [92]

The aim of model number V is to describe the pollution spreading in a groundwater reservoir bound at the top. The pollutant mass enters a planar source of pollution with the area A = Lx × Ly. This source of pollution is located at a permeable edge on the top of the saturated zone, and it is parallel to the flow direction (see Figure 4.5) [93]. The conservation of mass of contaminant is described by the contaminant transport equation [93]:

$$R\frac{\partial C_c}{\partial t} + u\frac{\partial C_c}{\partial t} - D_x\frac{\partial^2 C_c}{\partial x^2} - -D_y\frac{\partial^2 C_c}{\partial y^2} - D_z\frac{\partial^2 C_c}{\partial z^2} + \lambda \times C_c = 0 \tag{4.6}$$

with:

$$D_x = \alpha_l \times u \tag{4.7}$$

$$D_y = \alpha_t \times u \tag{4.8}$$

$$D_y = \alpha_v \times u \tag{4.9}$$

where:

- α_l **[L]** is the longitudinal dispersivity (x direction). It is an essential parameter in the analysis of the contaminants' spreading in one dimension because it describes the breakthrough of a contaminant to a point of compliance (POC), i.e. the point at which the chemical concentration is wanted to be below the groundwater guidelines [94];
- α_t **[L]** is the transversal dispersivity (y direction) in the water phase;
- α_v **[L]** is the vertical dispersivity (z direction) in the water phase. It is normally very low;
- $\mathbf{C}_c$ $[\mathbf{M/L^3}]$ is the contaminant concentration;
- $\mathbf{D}_x$ $[\mathbf{L^2/T}]$ is the longitudinal dispersion coefficient (x direction);
- $\mathbf{D}_y$ $[\mathbf{L^2/T}]$ is the transversal dispersion coefficient (y direction);
- $\mathbf{D}_z$ $[\mathbf{L^2/T}]$ is the vertical dispersion coefficient (z direction);
- λ **[1/T]** is the 1st order degradation rate. The degradation is assumed to occur only in the water phase [93];
- **R** **[-]**is the retardation coefficient (see Chapter 2.3). As the model is stationary, the retardation does not affect the resulting concentration [93];
- **u** **[L/T]** is the groundwater velocity in the x direction (see Figure 4.5).

The reactions described in Equation 4.6 occur only in the dissolved phase [92]. The solution to Equation 4.6 is a 3D steady-state analytical solution, which includes dispersion and advection in the aquifer. It is provided by the Danish Ministry of Environment and gives as result the concentration for a point source located at (x′y′) [93]:

$$C_c(x,y,z) = C_0 + \int_{-L_y/2}^{L_y/2} \int_{o}^{min(x,L_x)} \frac{2M_D}{(L_x \times L_y) \times 4\pi n\gamma \times \sqrt{D_y D_z}} \exp(\frac{u(x-x')}{2D_x} - \frac{\beta\gamma}{2D_x}) dx' dy' \tag{4.10}$$

with:

$$\beta = (u^2 + 4D_x\lambda)^{1/2} \tag{4.11}$$

$$\gamma = \sqrt{(x-x')^2 + \frac{D_x}{D_y}(y-y')^2 + \frac{D_x}{D_z}z^2} \tag{4.12}$$

where:

- $\mathbf{C}_0$ $[\mathbf{M/L^3}]$ is the source concentration;
- $\mathbf{L}_x$ **[L]** is the length of the contaminant source in the x direction;

- $\mathbf{L}_y$ **[L]** is the length of the contaminant source in the y direction;

- $\mathbf{M}_D$ **[M/T]** is the mass discharge, given by the product of the area (i.e. $L_x \times L_y$), the concentration C_0 and the infiltration flux I [L/T], which is zero in the contaminant source but occurs for x > Lx [93];

- **z** **[L]** is the depth below the top of the aquifer.

The integration considers the principle of superposition (i.e., by definition, the effective response of two or more stimuli is the sum of the responses that each stimulus would cause individually), which allows obtaining the cumulative effect of the source over the area A = $(0 < x' < L_x, -\frac{L_y}{2} < y' < \frac{L_y}{2})$. In addition, because it is only necessary to integrate for point sources upstream of x, the upper x limit of the integration is min(x, L_x) [93].

4.4.2 Set-up of the GrundRisk simulations

The GrundRisk analysis was only executed on the polycyclic aromatic hydrocarbons (PAHs). In order to work correctly, GrundRisk needs concentrations detected in the source area of the aquifer (i.e. the origin of the contamination) and the information about the area itself (e.g. porosity and groundwater velocities). This information was not available for the area affected by the chlorophenols (CPs).

Figure 4.6 describes the path completed by the PAHs from the wood impregnation plant to the water intake plant, whose distance was estimated to be of (approximately) 2.1 km. As Figure 4.7 shows, the velocities along the pathway are not constant but vary between 0.20 and 2.3 m/day, with the highest values reached in the main groundwater flow path, i.e. between the two bays (between 1.6 and 2.3 m/day). GrundRisk is a very simple model and does not take into account variation of groundwater. As it can be seen from Figure 4.6 and 4.7, before the azure circle, the groundwater flow is different (smaller) in comparison to the main groundwater flow path around the two bays (i.e. from the blue circle to the water intake plant). As a consequence, the simulations on the PAHs were only executed in the pathway going from the wood impregnation plant to the azure circle, i.e. close to the source area (look at Figure 4.6). The azure circles was therefore defined as the point of compliance (POC). The path has approximately a length of 500 m and the groundwater velocity varies between 0.5 and 1.0 m/day. In addition, because the goal of the analysis was to check if the groundwater guidelines were met at the POC, it was decided to focus the modeling only on the results in the downstream direction (along the aquifer), and not to consider the ones obtained along the longitudinal and vertical direction (i.e. y and z direction). Also, no detail of the Matlab code could be inserted in the Master's Thesis because the software is still under development and it did not have any official on-line release.

Table 4.5 and 4.6 specifies all the variables that were inserted in GrundRisk as inputs. The values of the octanol water partition coefficient K_{ow} were taken from a study conducted by Mackay et al. [95]. The distribution coefficient K_d was defined according to the Abdul's formula (see Chapter 2.3). The first order degradation rate was calculated by taking into account its half life ($\lambda = \frac{1}{t_{1/2}}$), which is determined from the most important degradation processes. Despite there is degradation of the contaminants in the site, it was not possible to collect any information about the degradation of the contaminants in the Pursiala aquifer. Therefore, in order to estimate the λ values, it was decided to take as a reference a study conducted by Howard et al. [96] on the degradation of the chemicals. On the basis of this study, hydrolysis and biodegradation were considered as the principal degradation means, with no consideration for processes such as volatilization and adsorption [96]. In this study, the $t_{1/2}$ values of the contaminants were estimated in groundwater and in aerobic and anaerobic aqueous systems. Due to the many factors affecting the biodegradation (e.g. the number of microorganisms in the soil and the redox conditions), it was not possible to define an exact value of the $t_{1/2}$. Consequently, GrundRisk was modelled by looking at all the $t_{1/2}$ values obtained by Howard et al. The $t_{1/2}$, which best modelled the concentrations of the POVET database through GrundRisk, was chosen.

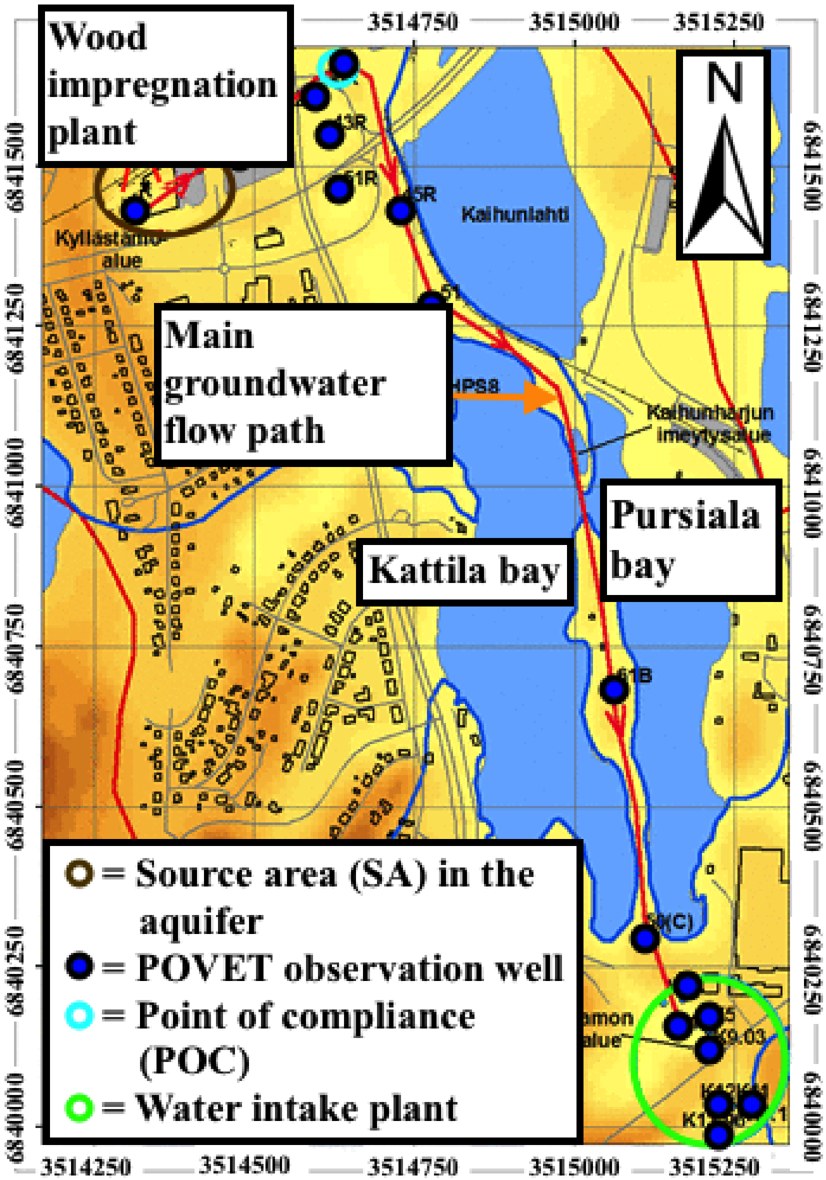
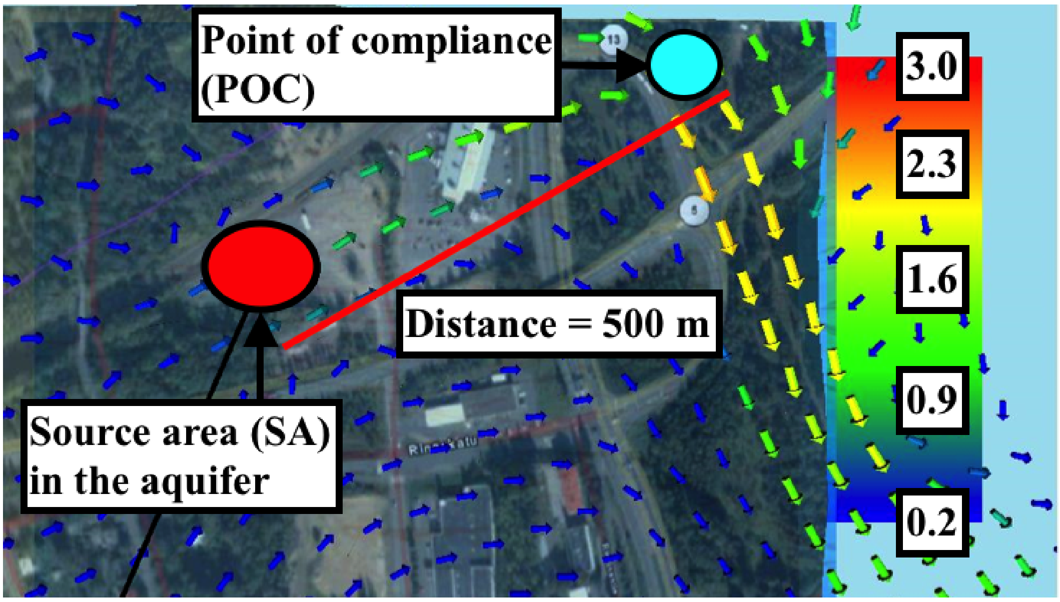


Figure 4.6: PAH path from the wood impregnation plant to water intake plant [56]



The colour of the arrows expresses the velocity in m/day. The red circle is the source area (SA) in the aquifer, i.e. where the GrundRisk simulations start, while the azure circle is the point of compliance (POC), i.e. the last point of the simulations

Figure 4.7: Groundwater velocity from the wood impregnation plant [56]

A series of attempts with fictitious concentrations and values of the GrundRisk variables were executed in order to understand the variables mostly influencing the system. A high variation of the results was given by varying the degradation rate λ, the source area A, the dispersivities D, the groundwater velocity u and the porosity n. In particular, λ revealed to be the parameter influencing the most in GrundRisk. In addition, it was discovered that modifying the sorption parameters did not affect the simulations. This aspect of GrundRisk was not surprising because GrundRisk is a steady-state model and time is not considered. Sorption affects the time needed to reach the steady state in a transient solution increasing the time by a factor of R (see Chapter 2.3). The simulations in GrundRisk were executed in order to obtain the same (or at least similar) concentrations detected in the POVET wells installed around the wood impregnation plant (see Table 3 in Appendix 2 for the PAH concentrations detected by the POVET wells). GrundRisk was therefore calibrated with the most influencing GrundRisk parameter, i.e. λ.

It was decided to set a number of 30 simulations. In the first 10, by varying the degradation rate λ (i.e. the most influencing parameter), it was found the value of λ and the other parameters that produced a similarity between the GrundRisk results and the concentrations detected by the POVET wells. In the remaining 20 simulations, the "optimal values" of the parameters were slightly altered (i.e. very low standard deviation between them) in order to keep the similarity with the POVET database. Figure 4.8 summarizes the main steps of the GrundRisk procedure. Table 5 in Appendix 2 shows the values of the variables used for the PAH assessment.

Table 4.5: Variables inserted in GrundRisk - first part

Variable	Meaning
α_l [m]	Longitudinal dispersivity in the x direction
α_t [m]	Transverse dispersivity in the y direction
α_v [m]	Vertical dispersivity in the z direction
B [m]	Aquifer thickness
C_0 [μg/l	Concentration in the source area
f_{oc} [-]	Fraction of organic carbon
K_{ow} [cm^3/g]	Octanol water partition coefficient
I [m/day]	Infiltration
L_x [m]	Length of the contaminant source in the x direction
L_y [m]	Length of the contaminant source in the y direction
λ [day^{-1}]	First order degradation rate
n [-]	Porosity
u [m/day]	Groundwater velocity in the x direction
ρ_b [g/cm^3]	Bulk density

Table 4.6: Variables inserted in GrundRisk - second part

Variable	Meaning	Formula
A [m^2]	Source area	Lx $\times$ Ly
D_x [m^2/day]	Longitudinal dispersion coefficient	$\alpha_l \times$u
D_y [m^2/day]	Transverse dispersion coefficient	$\alpha_t \times$u
D_z [m^2/day]	Vertical dispersion coefficient	$\alpha_v \times$u
K_d [cm^3/g]	Distribution coefficient	$f_{oc} \times 10^{1.04 \times log(K_{ow})-0.84}$
M_d [g/day]	Mass discharge	I x A x (C_0)
R [-]	Retardation factor	$1 + (\frac{K_d \times \rho_b}{n})$

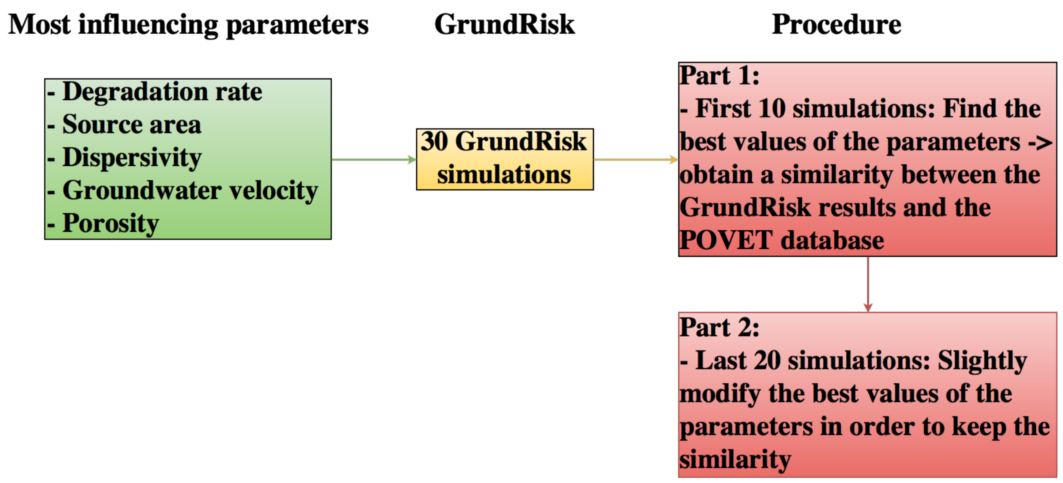


Figure 4.8: Main steps of the GrundRisk procedure

4.5 Assessment of human exposure

When considering groundwater, there are different ways through that human beings can enter in contact with it. Generally, ingestion is considered as the most significant exposure route. Many chemicals (such as mono- and dichlorophenols) are volatile and it is necessary to asses the risk for dermal and inhalation exposure [97]. Figure 4.9 shows the conceptual model considered for this project.

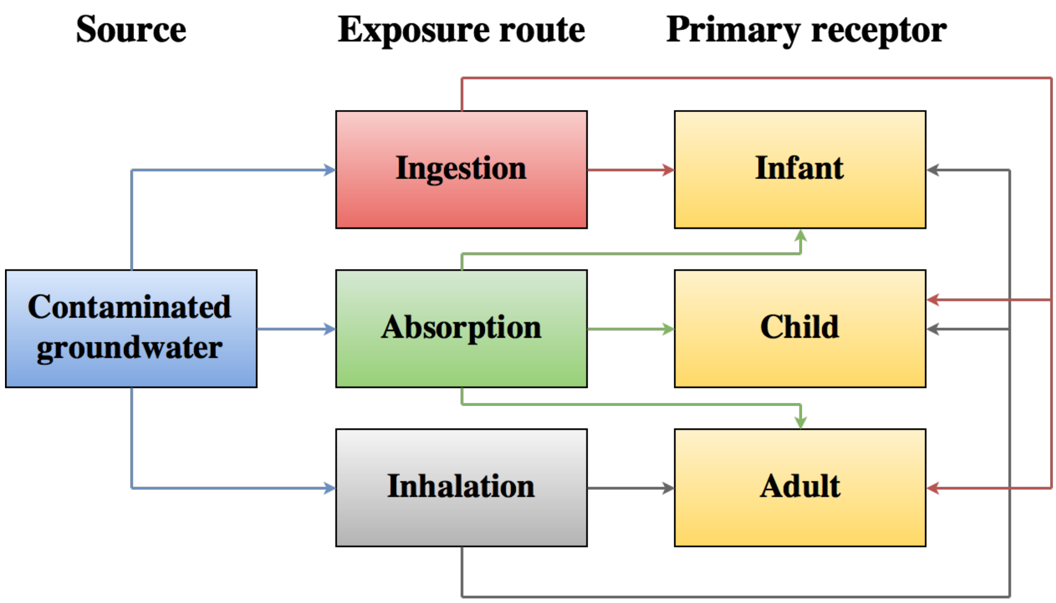


Figure 4.9: Generic conceptual model describing the formation of risks related to contaminated groundwater

Because of the missing information regarding the concentration of the CPs and PAHs in the air, it was not possible to calculate the exposure through the inhalation route. It could be calculated from the groundwater concentrations based on Henry's law constant (see Chapter 3.2), but it was assumed to be not an important exposure route due to the not so high concentrations in the source area in the aquifer.

Generally, Equation 4.13 is used to estimate the human exposure resulting from contact with a contaminated medium [98]:

$$D = \frac{C_c \times IR \times AF \times EF}{BW} \tag{4.13}$$

where:

- **AF** [%] is the absorbed fraction, i.e. the total amount of a substance inhaled, contacted or ingested that actually enters the bloodstream and can harm;
- **BW** [kg] is the body weight of a target group;
- **C$_c$** [**mg/kg in soil, mg/l in water or mg/m^3 in air**] is the contaminant concentration;
- **ED** [year] is the exposure duration, which, by definition, is indicated as the time of contact between a chemical and a human recipient;

- **EF [-]** is the exposure factor, which is referred to the exposure of the contaminant (it is a daily exposure if equal to 1). Normally, is calculated from Equation 4.14 [98]:

$$EF = \frac{F \times ED}{AT} \tag{4.14}$$

  The F [day/year] is the frequency of exposure and AT [-] is the averaging time, which is equal to ED × 365 days/year. Consequently, EF = $\frac{F}{365\ days/year}$

- **IR [mg/day, l/day]** is the intake rate of the contaminant medium.

Regarding the ingestion route, the preferred way for estimating the contamination of drinkable water is through the analysis of the concentration in tap water. If these data are anyway missing, the analysis is executed on the monitoring wells [97]. Equation 4.15 was used to determine dose through the ingestion route $D_{Ingestion}$ [mg/kg/day] [98]:

$$D_{Ingestion} = \frac{C_c \times IR \times EF}{BW} \tag{4.15}$$

The C_c is in mg/l and IR in l/day (liters of water per day). The value of C_c, for the CPs, were taken from Table 4.3, and for the PAHs from the results of the GrundRisk simulations (see Chapter 5.2). The standard default values for the ingestion exposure are showed in Table 6 in Appendix 4. The values of the ingestion reference dose $RfD_{Ingestion}$ were taken from the Integrated Risk Information System (IRIS), which is a database maintained by US EPA and containing all the information regarding possible hazards to human health of the chemicals found in nature [99]. It is a chronic RfD, i.e. a reference dose used for long-term exposure (most interesting than the short-term exposure). Table 4.7 collects all the $RfDs_{Ingestion}$ for CP and PAHs. No $RfD_{Ingestion}$ was found for 2,4,6-trichlorophenol, chrysene and phenathrene.

Normally, the dermal absorption of contaminants in water occurs during showering, bathing or outdoor activities such as swimming. The impact of a chemical on the human body is related to the characteristic of the substance: its physicochemical properties, such as molecular weight (high influence for low weights) or hydrophobicity (high influence for high values), have a high impact on the permeability of the skin [97]. The dose through dermal route D_{Dermal} [mg/kg/day] was determined according Equation 4.16 [98]:

$$D_{Dermal} = \frac{C_c \times P \times BSA \times ET \times CF \times EF}{BW} \tag{4.16}$$

where [97]:

- **BSA [cm^2]** is the body surface area;
- **CF [1 l/1000 cm^3]** is the conversion factor;
- **ET [hour/day]** is the exposure time. It is strictly related to seasonal factors, age and geographical factors. US EPA established average showering and bathing times for adults and children, i.e., respectively, 12 and 20 minutes [100];
- **P [cm/hour]** is the dermal permeability coefficient for a chemical. By using this coefficient, the dermal absorption of a chemical, from water, can be estimated. It

has a wide range and it is important to take into account its source of reference because the coefficient derived from animal studies may not be suitable for human assessments due to the substantial differences in skin permeability.

Table 4.7: Ingestion Reference Dose $RfD_{Ingestion}$ of Chlorophenols (CPs) and Polycyclic Aromatic Hydrocarbons (PAHs) [99]

Chemical	**$RfD_{Ingestion}$ [mg/kg/day]**
2-CP	5.0E-03
2,4-DCP	3.0E-03
2,4,6-TCP	-
2,3,4,6-TeCP	3.0E-02
PCP	5.0E-03

Chemical	**$RfD_{Ingestion}$ [mg/kg/day]**
Acenaphthene	6.0E-02
Anthracene	3.0E-01
Benzo(a)pyrene	3.0E-04
Chrysene	-
Fluoranthene	4.0E-02
Fluorene	4.0E-02
Naphthalene	2.0E-02
Phenanthrene	-
Pyrene	3.0E-02

Table 7 in Appendix 4 shows the default values of the body surface area (BSA). The dermal reference dose RfD_{Dermal} was calculated by using Equation 4.17 [101]:

$$RfD_{Dermal} = RfD_{Ingestion} \times GI \tag{4.17}$$

GI [%] is the gastrointestinal factor, which is used to make the conversion.

Table 4.8 shows the dermal RfD_{Dermal} for the CPs and the PAHs (daily intake reference doses), together with the P and the GI factor that derive, respectively, from US EPA [102] and from a consulting company named GSI Environmental Inc. [103]. Between the CPs, the P could not be found for 2,3,4,6-TCP. On the other hand, for the PAHs, the GI factor is the same for all the compounds, and the P was not found for acenapthene, anthracene, fluorene and pyrene. In addition, because no ingestion RfD was found for chrysene and pyrene (see Table 4.7), it was not possible to determine their dermal RfDs.

To determine the non-carcinogenic risks for human beings, the Hazard Quotient HQ is calculated according to Equation 4.18 [2]:

$$HQ = \frac{D}{RfD} \tag{4.18}$$

Table 4.8: Dermal Permeability Coefficient (P), Dermal Reference Dose (RfD_{Dermal}) and Gastrointestinal Factor (GI) of Chlorophenols (CPHs) and Polycyclic Aromatic Hydrocarbons (PAHs)[103] [102]

Chemical	**P [cm/hour]**	**GI [-]**	**RfD_{Dermal} [mg/kg/day]**
2-CP	8.0E-03	8.0E-01	4.0E-03
2,4-DCP	2.1E-02	8.2E-01	2.5E-03
2,4,6-TCP	3.5E-02	5.0E-01	-
2,3,4,6-TeCP	-	5.0E-01	1.5E-02
PCP	3.9E-01	7.6E-01	3.8E-03

Chemical	**P [cm/hour]**	**GI [-]**	**RfD_{Dermal} [mg/kg/day]**
Acenaphthene	-	8.9E-01	5.3E-02
Anthracene	-	8.9E-01	2.7E-01
Benzo(a)pyrene	7.0E-01	8.9E-01	2.7E-04
Chrysene	4.7E-01	8.9E-01	-
Fluoranthene	2.2E-01	8.9E-01	3.6E-02
Fluorene	**-**	8.9E-01	3.6E-02
Naphthalene	4.7E-02	8.9E-01	1.8E-02
Phenanthrene	1.4E-01	8.9E-01	-
Pyrene	-	8.9E-01	2.7E-02

D is the exposure dose calculated by Equations 4.15 and 4.16 and RfD is the reference dose for the ingestion and the dermal exposure route. If HQ is ≤ 1 (i.e. the acceptable level for non-carcinogenic effects), no adverse health effect is expected [2].

The total non-carcinogenic risk for an exposure route is evaluated by the sum of the HQs for each chemical (HQ_i): the Hazard Index HI. It is calculated by Equation 4.19 [104]:

$$HI = \Sigma HQ_i \tag{4.19}$$

The cumulative HI is given by the sum of the Hazard Indexes from all the scenario-specific exposure routes:

$$Cumulative\ HI = \Sigma HI_j \tag{4.20}$$

HI_j is the Hazard Index for a specific exposure route.

No analysis was executed on carcinogenic risks. Further comments about this decision are discussed in Chapter 6.3.

5. Results

The chapter reports the results of the procedures adopted in the Master's Thesis: the DRASTIC methodology (see Chapter 5.1), the GrundRisk simulations (see Chapter 5.2) and the human health risk assessment executed on the chemicals (see Chapter 5.3).

5.1 Vulnerability of the aquifer

The vulnerability of the aquifer was analyzed in order to understand the risk of groundwater contamination due to the industrial activities at Mikkeli. The DRASTIC method was executed by taking into account the hydrogeological information of the two study areas (see Table 3.1). The DVI index was calculated according to Equation 4.2. In addition, by using Equation 4.3, 4.4 and 4.5, a sensitivity analysis was conducted in order to obtain a better understanding of the vulnerability of the aquifer. This section is divided into three parts: the results of the vulnerability of the aquifer in the area around the wood impregnation plant and in the area around the sawmill, and a summary of the key results obtained in the section.

5.1.1 Area affected by the wood impregnation plant

Table 5.1 shows that there are three parameters with two different ratings. Because the main goal of the analysis was to understand the range of vulnerability of the aquifer, the analysis was executed only on the lowest and the highest DVI value which can be obtained from these parameters. Therefore, the DVI index can either be 145 or 152. The difference is very small (about 5%), i.e. the difference in the ratings does not affect the value of the DVI index. Considering that the generic DVI range goes from 31 to 226 (see Chapter 4.3), it could be stated that the aquifer is quite vulnerable.

Table 5.1: Parameters' weights for the DRASTIC analysis of the area around the wood impregnation plant

Parameter	**Parameter range**	**Parameter rating**	**Parameter weight**	**Parameter total weight**
D	10 - 15 m	1	5	5
R	280 - 330 mm/a	9	4	36
A	Alluvium	10	3	30
S	Gravel	8	2	16
T	0 - 2 %	9 or 10	1	9 or 10
I	Sand and gravel	8	5	40
C	60 - 80 m/d	3 or 5	3	9 or 15
DVI = 145 or 152				

The parameter having the highest total weight is the impact of soil type of the vadose zone I, followed by the net recharge R and the aquifer soil type A. The depth to the water table D and the topography T provide the least total weight to the vulnerability of the aquifer.

The map removal sensitivity analysis was conducted by removing one parameter (n) per time (see Equation 4.3) in order to see the variation of the DVI index. As it can be seen from Table 5.2, the highest variation of DVI belongs to the removal of the impact of the soil type of the vadose zone I for the lowest and the highest rating. To be precise, there is a DVI decrease of 38% and 35% from the original indexes. In addition, the removal of the net recharge R and the aquifer soil type A from the computation caused a high decrease on the DVI. The analysis continued with the removal sensitivity index of more than one parameter. As expected, the more the parameters with a high weight on the DVI are removed, the higher is the variation between the indexes increases (see at Table 5.1).

Table 5.2: Results of the map removal sensitivity analysis for the area around the wood impregnation plant. DVI' is the DRASTIC index calculated with less parameters and SI is the sensitivity index

		Lowest rating		**Highest rating**	
Removed parameter	**Remaining parameters (N'_p)**	**New index DVI′**	**SI [%]**	**New index DVI′**	**SI [%]**
D	6	140	1.8	149	1.8
R	6	109	1.8	118	1.6
A	6	115	1.1	124	0.9
S	6	129	0.5	136	0.6
T	6	136	1.3	144	1.3
I	6	105	2.2	114	2.1
C	6	136	1.3	139	0.7

		Lowest rating		**Highest rating**	
Removed parameter	**Remaining parameters (N'_p)**	**New index DVI′**	**SI [%]**	**New index DVI′**	**SI [%]**
D	6	140	1.8	147	1.8
DT	5	131	3.8	137	3.7
DTC	4	122	6.7	122	5.8
DSTC	3	106	10.1	106	8.9
DASTC	2	76	11.9	76	10.7
DRASTC	1	40	13.3	40	12.1

The single parameter sensitivity analysis (see Equation 4.4 and 4.5) was applied in order to analyze the influence of each parameter in the DVI index. The analysis is summarized in Table 5.3. The net recharge R became, together with I (which maintained its high weight), the parameter having the major weight on the vulnerability index. In addition, A increased its weight of, respectively, about 56% and 50% for the lowest and highest rating. On the other hand, the depth to water table D highly decreased its weight (for the two ratings of about 85%), becoming a not so relevant parameter in the study of the vulnerability of the aquifer. The soil type S and the topography T slightly increased for the two ratings, while the hydraulic conductivity C slightly decreased in comparison to D.

Table 5.3: Results of the single parameter sensitivity analysis for the area around the wood impregnation plant

Lowest rating

	Theoretical		**Effective**	
Parameter	**Parameter weight**	**W [%]**	**W [%]**	**Parameter weight**
D	5	21.7	3.4	0.8
R	4	17.4	24.8	5
A	3	13.0	20.7	4.8
S	2	8.7	11	2.5
T	1	4.3	6.2	1.4
I	5	21.7	27.6	5
C	3	13.0	6.2	1.4

Highest rating

	Theoretical		**Effective**	
Parameter	**Parameter weight**	**W [%]**	**W [%]**	**Parameter weight**
D	5	21.7	3.3	0.8
R	4	17.4	23.7	5
A	3	13.0	19.7	4.5
S	2	8.7	10.5	2.4
T	1	4.3	6.6	1.5
I	5	21.7	26.3	5
C	3	13.0	9.9	2.3

According to these new weights of the parameters, it was possible to define the new DVI indexes. By looking at Table 5.4, the DVI index, according to the effective weights, is either equal to 170.6 and 176.4. This means that the change was not so high, but the aquifer (slightly) increased its vulnerability. To be precise, the initial and the modified DVI index differ, according to the lowest and highest rating, of about 17% and 16% (see Table 5.1 and 5.4). In addition, even in this case the difference between the two DVIs is very low, i.e. of about 3%.

Table 5.4: Modified DRASTIC index according to the effective parameters' weights of the two ratings for the area around the wood impregnation plant

Parameter	**Parameter range**	**Parameter rating**	**Parameter weight**	**Parameter total weight**
D	10 - 15 m	1	0.8	0.8
R	280 - 330 mm/a	9	5	45
A	Alluvium	10	4.8 or 4.5	48 or 45
S	Gravel	8	2.5 or 2.4	20 or 19.2
T	0 - 2 %	9 or 10	1.4 or 1.5	12.6 or 15
I	Sand and gravel	8	5	40
C	60 - 80 m/d	3 or 5	1.4 or 2.3	4.2 or 11.5
DVI = 170.6 or 176.4				

Figure 5.1 visualizes in details the DVI indexes according to the original and the modified DRASTIC model.

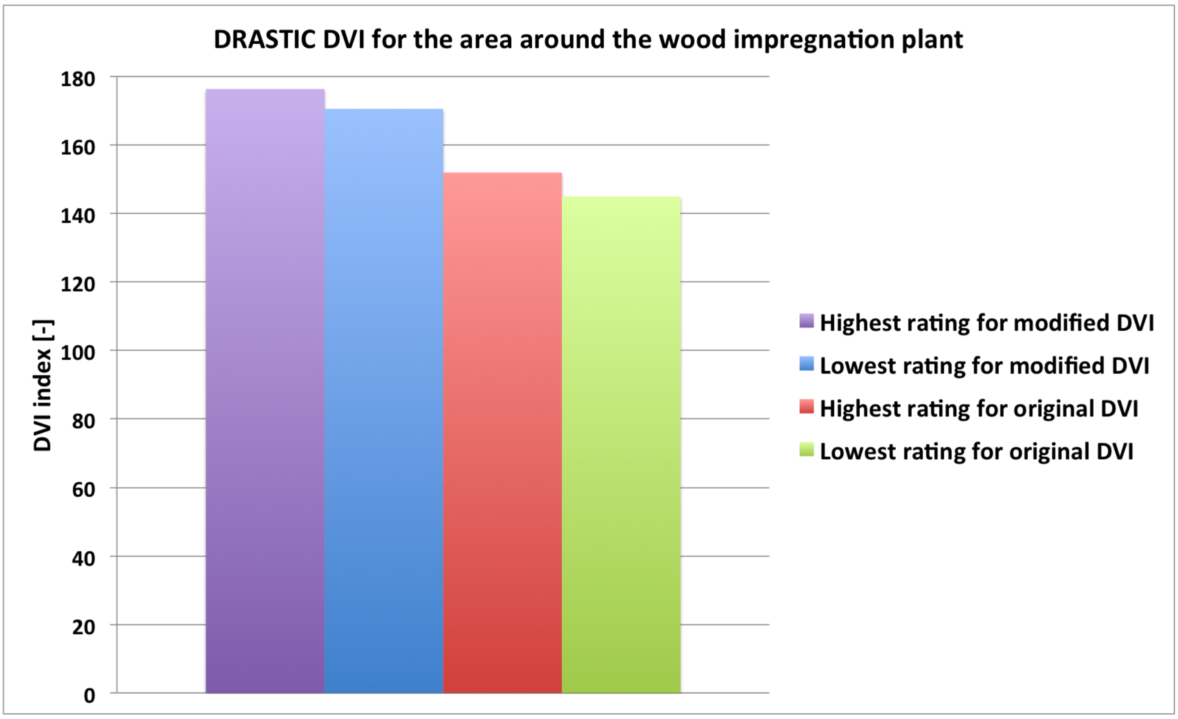


Figure 5.1: DRASTIC DVI indexes for the area around the wood impregnation plant

5.1.2 Area affected by the sawmill

A similar DRASTIC analysis used in Chapter 5.1.1 was used as well for the area around the sawmill. According to Table 5.5, the minimum and the maximum DVI index are, respectively, 143 or 168 in this area. This means that, in comparison to the previous case (see Table 5.1), the vulnerability in this part of the aquifer is slightly higher. This is mostly due to the groundwater table D, which is less deep in this case and, consequently, makes the aquifer more vulnerable (see Table 5.5). The difference between the two DVIs in this case is of about 18%. It is not so high, but the ratings have a higher influence on the vulnerability than before. The parameter having the highest weight is the impact of the soil type of the vadose zone I.

The map removal sensitivity analysis was executed with Equation 4.3. The results are reported in Table 5.6. As previously, the exclusion of more than one parameter caused a higher increase in the variation between the indexes. Just like the PAH case, the highest modification of DVI belonged, for the lowest and the highest rating, to the removal of the impact of the soil type of the vadose zone I, with a DVI decrease of 39% and 34% from the original indexes. The variation of vulnerability index seemed also to be relatively sensitive to the removal of the net recharge R from the computation (as well as the aquifer soil type A).

Table 5.5: Parameters' weights for DRASTIC analysis of the area around the sawmill

Parameter	Parameter range	Parameter rating	Parameter weight	Parameter total weight
D	5 - 10 m	1 or 3 or 5	5	5 or 15 or 25
R	250-300 mm/a	8 or 9	4	32 or 36
A	Alluvium	10	3	30
S	Gravel-sand	9	2	18
T	0 - 2 %	9 or 10	1	9 or 10
I	Sand and gravel	8	5	40
C	30 - 50 m/d	3	3	9
DVI = 143 or 168				

Table 5.6: Results of the map removal sensitivity analysis for the area around the sawmill. DVI' is the DRASTIC index calculated with less parameters and SI is the sensitivity index

		Lowest rating		**Highest rating**	
Removed parameter	**Remaining parameters (N'_p)**	**New index DVI′**	**SI [%]**	**New index DVI′**	**SI [%]**
D	6	138	1.8	143	0.1
R	6	111	1.3	132	1.2
A	6	113	1.12	138	0.6
S	6	125	0.28	150	0.6
T	6	134	1.33	158	1.4
I	6	103	2.3	128	1.6
C	6	134	1.3	159	1.5

		Lowest rating		**Highest rating**	
Removed parameter	**Remaining parameters (N'_p)**	**New index DVI′**	**SI [%]**	**New index DVI′**	**SI [%]**
D	6	138	1.8	143	0.1
DT	5	129	3.8	133	1.5
DTC	4	120	6.7	124	4.2
DSTC	3	102	9.5	106	6.7
DASTC	2	72	10.9	76	8.3
DRASTC	1	40	13.7	40	9.5

The single parameter sensitivity analysis, for the two ratings, is summarized in Table 5.7. As before, Equation 4.4 and 4.5 were used for the calculations. Theimpact of the soil type of the vadose zone I maintained its weight, while the net recharge R became the parameter having a major weight on the vulnerability index. In addition, the aquifer soil type A highly increased of about 61% and 37% for the lowest and highest rating. On the other hand, the depth to water table D was the only parameter having a high decrease in weight for the lowest rating (a 84% reduction to be precise), which was not surprising considering its low DRASTIC weight (see Table 5.5).

Table 5.7: Results of the single parameter sensitivity analysis for the area around the sawmill

Lowest rating

	Theoretical		Effective	
Parameter	**Parameter weight**	**W [%]**	**W [%]**	**Parameter weight**
D	5	21.7	3.5	0.8
R	4	17.4	22.4	5
A	3	13.0	21	4.8
S	2	8.7	12.6	2.9
T	1	4.3	6.3	1.4
I	5	21.7	28	5
C	3	13.0	6.3	1.4

Highest rating

	Theoretical		Effective	
Parameter	**Parameter weight**	**W [%]**	**W [%]**	**Parameter weight**
D	5	21.7	14.9	3.4
R	4	17.4	21.4	5
A	3	13.0	17.9	4
S	2	8.7	10.7	2.5
T	1	4.3	6	1.4
I	5	21.7	23.8	5
C	3	13.0	5.4	1.2

According to the effective weights of the parameters, the DVI index is either equal to 171.7 or 182.1 (see Table 5.8). In comparison to Table 5.5, the difference from the original indexes is of about 20% and 8% for, respectively, the lowest and the highest rating. The change, especially for the highest rating, was not so high, but the sensitivity analysis (slightly) increased the vulnerability. In addition, the new indexes differ of about 6%.

Table 5.8: Modified DRASTIC index according to the effective parameters' weights of the two ratings for the area around the sawmill

Parameter	**Parameter range**	**Parameter rating**	**Parameter weight**	**Parameter total weight**
D	5 - 10 m	1 or 5	0.8 or 3.4	0.8 or 17
R	250 - 300 mm/a	8 or 9	5	40 or 45
A	Alluvium	10	4.8 or 4	48 or 40
S	Gravel-sand	9	2.9 or 2.5	26.1 or 22.5
T	0 - 2 %	9 or 10	1.4	12.6 or 14
I	Sand and gravel	8	5	40
C	30 - 50 m/d	3	1.4 or 1.2	4.2 or 3.6
DVI = 171.7 or 182.1				

As for the PAH case, Figure 5.2 shows the difference between the original and the modified DRASTIC indexes.

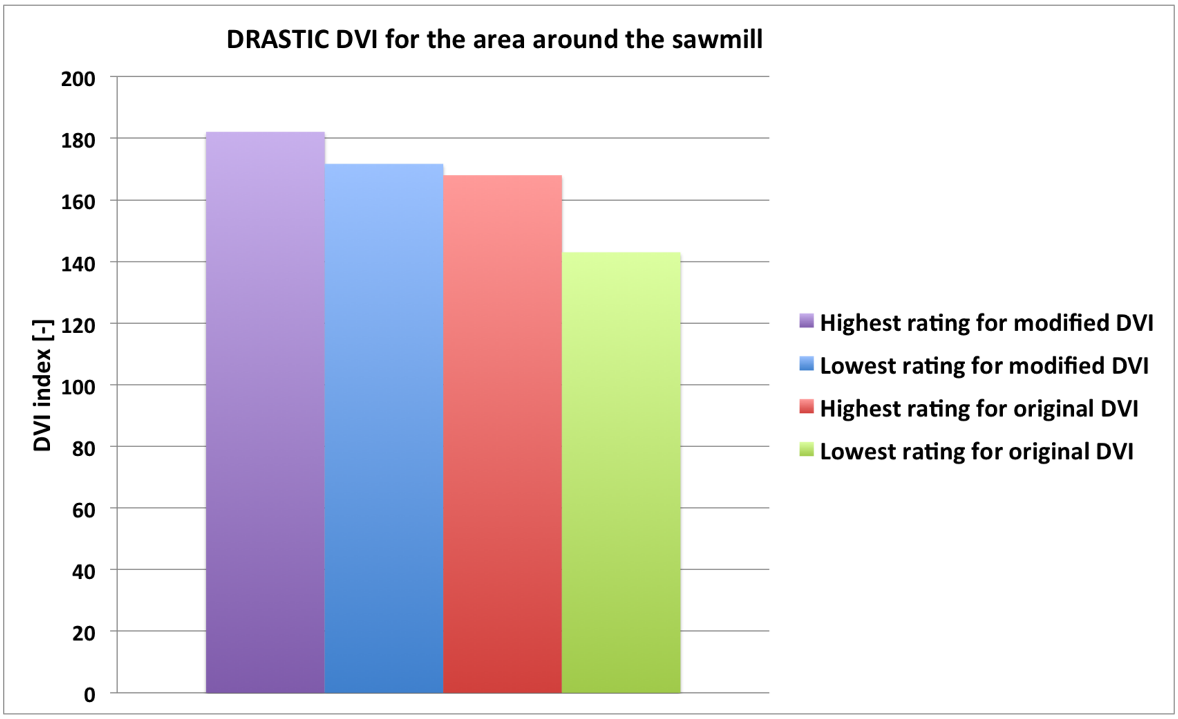


Figure 5.2: DRASTIC DVI indexes for the area around the sawmill

5.1.3 Summary of the DRASTIC analysis

Figure 5.3 shows the highest DVI indexes calculated for the two areas. The DVI is slightly higher for the sawmill area but, because the difference between them is very low (about 3%), the two areas have the same degree of vulnerability. In conclusion, considering that the DVI has a range between 31 to 226 (see Chapter 4.3), the aquifer presents a high vulnerability from contamination, i.e. it is very easy for the contaminants to reach the aquifer and to decrease the quality of groundwater. The risk is especially high for the area around the sawmill because it is very close to the water intake plant (see Figure 3.1).

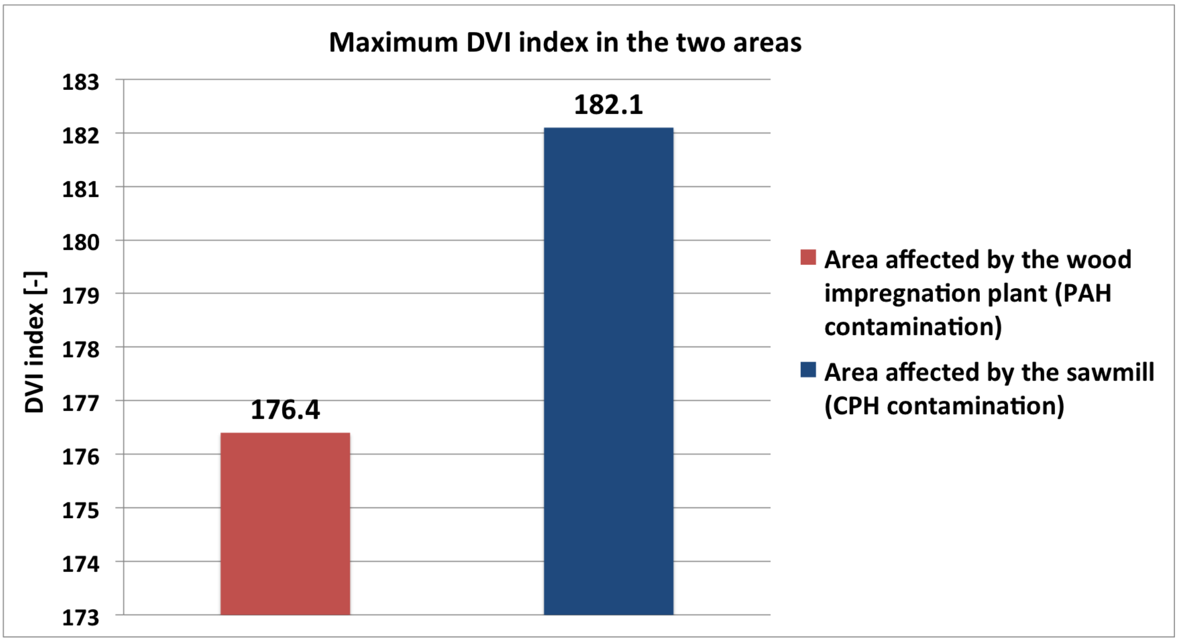


Figure 5.3: Maximum DVI index calculated for the area around the wood impregnation plant and the sawmill

5.2 Outcome of the modelling of dispersion in groundwater

The following section is divided into two parts: the first presents the results obtained from the GrundRisk simulations, which were only executed on the polycyclic aromatic hydrocarbons (PAHs), while the second is a summary containing the most important considerations driven from the results.

5.2.1 GrundRisk simulations of PAHs

The area around the wood impregnation plant, which was considered for the GrundRisk simulations, is showed in Figure 5.4. The results of the simulations were compared to the concentrations detected in the POVET groundwater wells around the area: 31R, 35R, 36R, 37R, 42R and 50R. Because no information could be found in the POVET database about well 36R, 37R and 38R, the comparison was executed only with the remaining wells (see Table 3 in Appendix 2). GrundRisk simulated the concentrations in the downstream direction (i.e. x-direction). A downstream length equal to 500 m, i.e. the distance between the point of compliance and the source area in the aquifer, was set for the simulation. The starting point is x = 0, i.e. the location of the source area. Each well was assumed to be in a specific position along the downstream: 31R at a distance of 25 m from the source area, 35R of 200 m, 42 R of 400 m and 50R of 500 m. Probably it is not the exact location of the wells, but it is a good approximation. Figure 5.4 visualizes the location of the four wells.

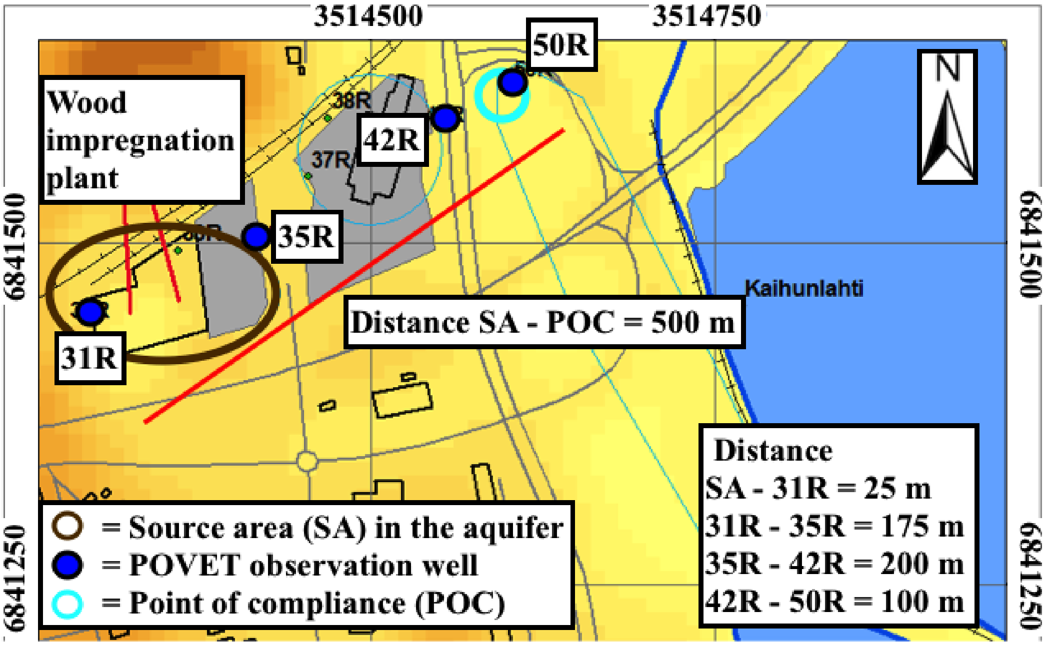


Figure 5.4: Details of the path considered for the GrundRisk analysis [56]

Table 4 in Appendix 2 shows the values of the GrundRisk variables that were used for the PAH case. Due to the high hydrophobicity of the PAHs, the distribution and the retardation coefficient have a very high value. Table 5.9 and 5.10 collect the results of the 30 GrundRisk simulations for the wells 31R, 35R, 42R and 50R (see Figure 5.4). According to them, benzo(a)pyrene and chrysene are the only compounds exceeding the groundwater guidelines (the latter for only well 31R). Therefore, it was decided to show the concentrations along the downstream direction of the aquifer (x- axis) of these two compounds in Figure 5.5 and 5.6. Through these graphs, it is possible to see the variation of the concentrations in each GrundRisk simulation. The last simulation, i.e. number 30 in the x-axis of Figure 5.5 and 5.6, was conducted at the point of compliance POC, which corresponds to the location of well 50R (see the blue circle in Figure 5.4). The simulations of the other PAH compounds were not relevant because, as it can be seen by Table 5.9, they gave concentrations below the groundwater guidelines. The graphs of these simulations are showed in Figure 3, 4, 5 and 6 in Appendix 3.

A series of considerations were drawn from the results obtained in Figure 5.5 and 5.6. The farer the well is from the source, the less sensible is the system to the modifications of the model. For all the PAH compounds, the variations of the input parameters of GrundRisk always caused high variations of the concentrations simulated in well 31R. The concentrations for benzo(a)pyrene are always above the guideline values, while chrysene exceeds the guideline for only well 31R (see the orange line in Figure 5.5 and 5.6). Comments about the simulations and the comparison with POVET are discussed in Chapter 6.2.

Table 5.9: Concentrations of Polycyclic Aromatic Hydrocarbons (PAHs) obtained in 30 GrundRisk simulations for well 31R, 35R and 42R. The value is highlighted in blue if it is above the groundwater guideline

Well 31R - 25 m from the source area (SA) in the aquifer

Chemical	Unit	Groundwater guideline	Max	Min	Mean	STDV	95% UCL
Acenaphthene	μg/l	400	1.9E+02	1.2E+01	5.8E+01	3.9E+01	1.4E+02
Anthracene	μg/l	2000	1.1E+01	1.6E+00	4.9E+00	2.7E+00	1.0E+01
Benzo(a)pyrene	μg/l	0.005	1.9E+01	4.0E-01	1.1E+01	4.0E-01	1.4E+00
Chrysene	μg/l	5	6.3E+00	1.4E+00	2.9E+00	1.4E+00	5.7E+00
Fluoranthene	μg/l	300	3.0E+01	6.1E+00	9.3E+00	5.9E+00	2.1E+01
Fluorene	μg/l	300	8.1E+01	8.4E+00	3.6E+01	1.5E+01	6.5E+01
Naphthalene	μg/l	300	2.9E+01	4.9E+00	2.1E+01	7.6E+00	3.6E+01
Phenanthrene	μglL	100	5.9E+01	1.4E+01	3.5E+01	1.1E+01	5.8E+01
Pyrene	μg/l	200	2.1E+01	4.5E+00	7.2E+00	4.1E+00	1.5E+00

Well 35R - 200 m from the source area (SA) in the aquifer

Chemical	Unit	Groundwater	Max	Min	Mean	STDV	95% UCL
Acenaphthene	μg/l	400	3.5E+01	1.3E+00	1.4E+01	9.4E+00	3.2E+01
Anthracene	μg/l	2000	5.5E+00	3.0E-01	2.1E+00	1.4E+00	5.1E+00
Benzo(a)pyrene	μg/l	0.005	5.0E-01	1.0E-01	2.0E-01	1.0E-01	4.0E-01
Chrysene	μg/l	5	1.6E+00	2.0E-01	8.0E-01	4.0E-01	1.6E+00
Fluoranthene	μg/l	300	7.1E+00	9.0E-01	2.8E+00	1.4E+00	5.5E+00
Fluorene	μg/l	300	1.8E+01	1.3E+00	5.8E+00	3.7E+00	1.3E+01
Naphthalene	μg/l	300	6.4E+00	9.8E-04	4.4E+00	2.4E+00	9.1E+00
Phenanthrene	μg/l	100	2.4E+01	4.1E+00	1.2E+01	4.9E+00	2.2E+01
Pyrene	μg/l	200	5.6E+00	4.0E-01	1.4E+00	1.4E+00	4.3E+00

Well 42R - 400 m from the source area (SA) in the aquifer

Chemical	Unit	Groundwater guideline	Max	Min	Mean	STDV	95% UCL
Acenaphthene	μg/l	400	1.6E+01	2.0E-01	4.1E+00	3.9E+00	1.2E+01
Anthracene	μg/l	2000	3.1E+00	1.0E-01	1.1E+00	8.0E-01	2.8E+00
Benzo(a)pyrene	μg/l	0.005	3.0E-01	1.0E-01	1.0E-01	1.0E-01	2.0E-01
Chrysene	μg/l	5	9.0E-01	1.0E-01	4.0E-01	3.0E-01	9.0E-01
Fluoranthene	μg/l	300	3.3E+00	4.0E-01	1.2E+00	6.0E-01	2.4E+00
Fluorene	μg/l	300	3.6E+00	1.0E-01	1.1E+00	9.0E-01	2.9E+00
Naphthalene	μg/l	300	1.7E+00	3.2E-08	9.0E-01	5.0E-01	2.1E+00
Phenanthrene	μg/l	100	1.1E+01	1.4E+00	5.1E+00	2.4E+00	9.9E+00
Pyrene	μg/l	200	3.1E+00	1.0E-01	7.0E-01	8.0E-01	2.2E+00

Table 5.10: Concentrations of Polycyclic Aromatic Hydrocarbons (PAHs) obtained in 30 GrundRisk simulations for well 50R. The value is highlighted in blue if it is above the groundwater guideline

Well 50R - 500 m from the source area (SA) in the aquifer (point of compliance, POC)

Chemical	Unit	Groundwater guideline	Max	Min	Mean	STDV	95% UCL
Acenaphthene	μg/l	400	1.2E+01	1.0E-01	2.5E+00	2.9E+00	8.4E+00
Anthracene	μg/l	2000	2.5E+00	1.0E-01	9.0E-01	7.0E-01	2.2E+00
Benzo(a)pyrene	μg/l	0.005	2.0E-01	1.0E-01	1.0E-01	1.0E-01	2.0E-01
Chrysene	μg/l	5	8.0E-01	1.0E-01	3.0E-01	2.0E-01	7.0E-01
Fluoranthene	μg/l	300	2.5E+00	3.0E-01	9.0E-01	4.0E-01	1.8E+00
Fluorene	μg/l	300	1.8E+00	1.0E-01	5.0E-01	5.0E-01	1.5E+00
Naphthalene	μg/l	300	9.0E-01	1.9E-10	5.0E-01	3.0E-01	1.1E+00
Phenanthrene	μg/l	100	8.4E+00	9.0E-01	3.6E+00	1.8E+00	7.2E+00
Pyrene	μg/l	200	2.4E+00	1.0E-01	5.0E-01	6.0E-01	1.8E+00

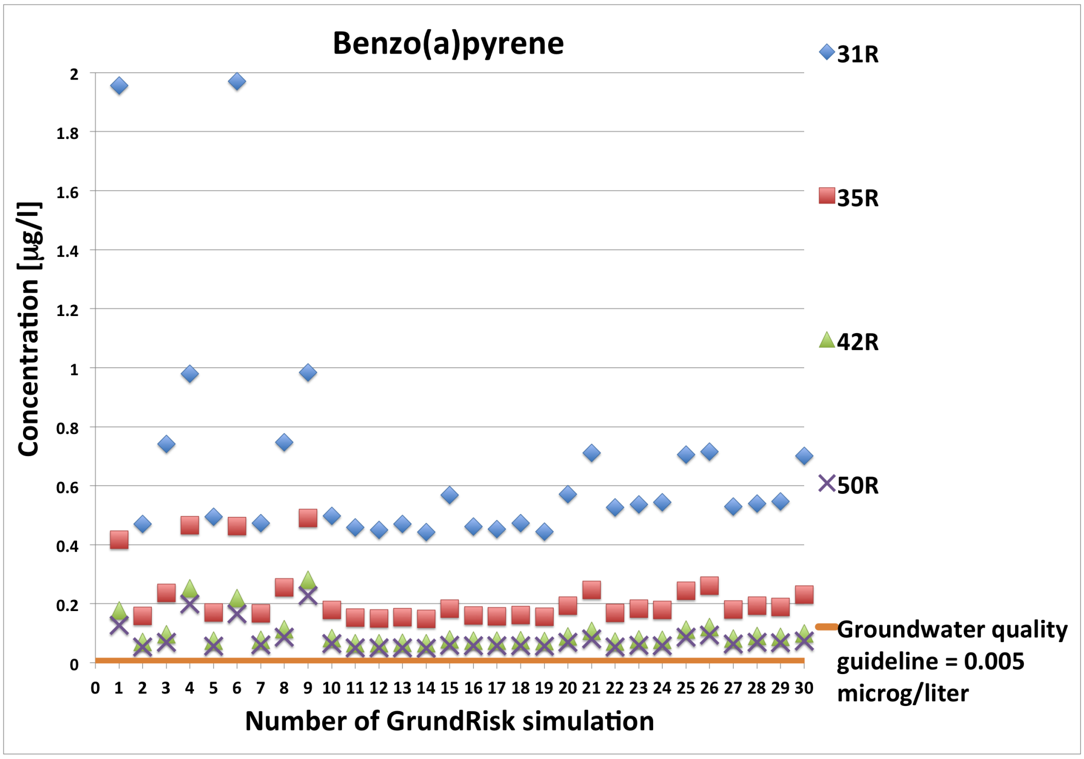


Figure 5.5: Benzo(a)pyrene concentrations obtained in each of the 30 GrundRisk simulations for well 31R, 35R, 42R and 50R. The number of the simulation is on the x-axis, and each point of the graph is the concentration obtained for the well in the simulation

Because it was not possible to make a simulation in the main groundwater flow path, the analysis in this path was conducted by looking at the concentrations detected in the wells of the POVET database. It was decided to focus only on three wells, i.e. 45R, 61B and K10, which are respectively located at the beginning, at the middle and at the end of the main groundwater flow path (see Figure 5.7). The analysis was executed in order to check if phenomena like dilution had an effect on the concentration of the chemicals.

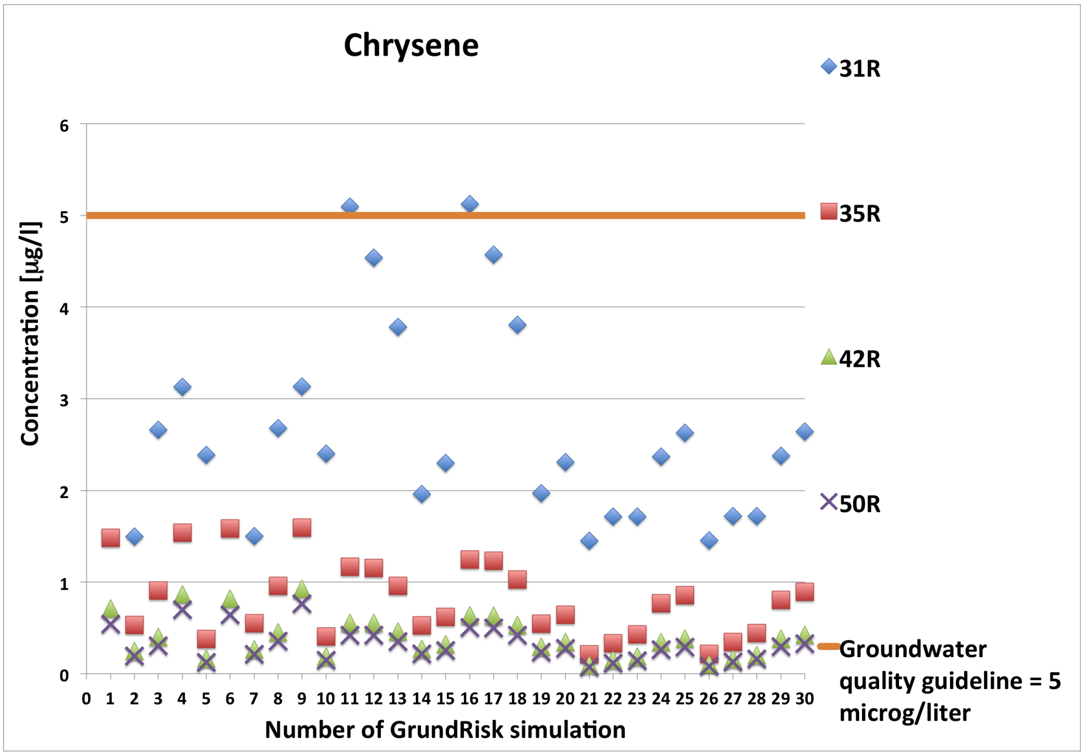


Figure 5.6: Chrysene concentrations obtained in each of the 30 GrundRisk simulations for well 31R, 35R, 42R and 50R. The number of the simulation is on the x-axis, and each point of the graph is the concentration obtained for the well in the simulation

As Figure 4.6 and 4.7 show, the main groundwater flow path is larger and presents a higher velocity than the path next to the wood impregnation plant. Results are reported in Table 5.11. Well 45R, i.e. at the beginning of the main groundwater flow path (see Figure 5.7), have higher concentrations in comparison to the other wells because it is closer to the wood impregnation plant. All the concentrations detected in well 45R are below the groundwater guidelines. The other two wells, in particular well K10, which is just before the water intake plant (see Figure 5.7), mostly have concentrations very small, i.e. < 0.1 μg/l.

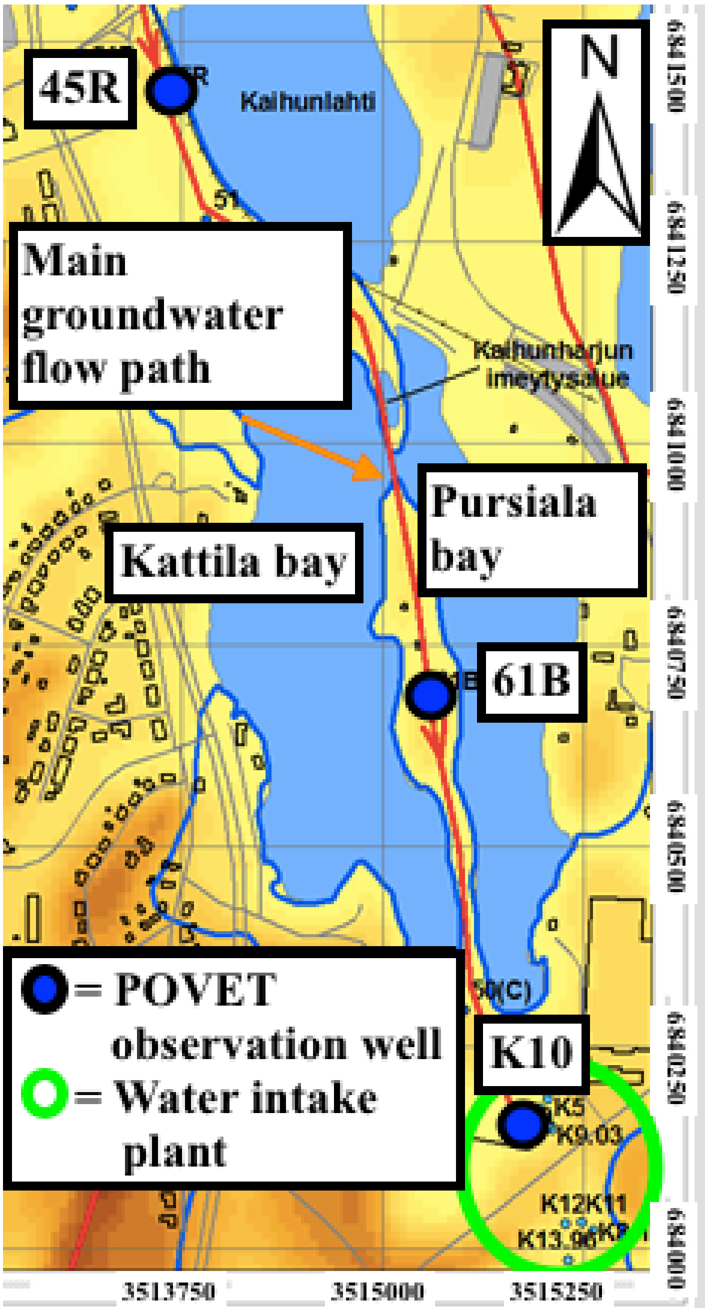


Figure 5.7: Main groundwater flow path [56]

Table 5.11: Concentrations of Polycyclic Aromatic Hydrocarbons (PAHs) detected in well 45R, 61B and K10 of the POVET database installed in the main groundwater flow path. All the values are below the groundwater guideline [86]

Well 45R - 6 samples

Chemical	**Unit**	**Drinking water**	**Max**	**Min**	**Mean**	**STDV**	**95% UCL**
Acenaphthene	μg/l	400	3.3E+01	1.5E+01	2.4E+01	6.4E+00	3.7E+01
Anthracene	μg/l	2000	1.0E-01	1.0E-01	1.0E-01	1.0E-02	1.0E-01
Benzo(a)pyrene	μg/l	0.005	< 1.0E-01	< 1.0E-01	< 1.0E-01	-	-
Chrysene	μg/l	5	< 1.0E-01	< 1.0E-01	< 1.0E-01	-	-
Fluoranthene	μg/l	300	1.0E+01	1.0E-01	1.7E+00	4.1E+00	9.8E+00
Fluorene	μg/l	300	1.4E+01	6.1E+00	1.0E+01	3.7E+00	1.8E+01
Naphthalene	μg/l	300	9.0E-01	2.0E-01	5.0E-01	3.0E-01	1.1E+00
Phenanthrene	μg/l	100	< 1.0E-01	< 1.0E-01	< 1.0E-01	-	-
Pyrene	μg/l	200	< 1.0E-01	< 1.0E-01	< 1.0E-01	-	-

Well 61B - 2 samples

Chemical	**Unit**	**Drinking water**	**Max**	**Min**	**Mean**	**STDV**	**95% UCL**
Acenaphthene	μg/l	400	3.1E+00	2.9E+00	3.2E+00	1.0E-01	3.3E+00
Anthracene	μg/l	2000	< 1.0E-01	< 1.0E-01	< 1.0E-01	-	-
Benzo(a)pyrene	μg/l	0.005	< 1.0E-01	< 1.0E-01	< 1.0E-01	-	-
Chrysene	μg/l	5	< 1.0E-01	< 1.0E-01	< 1.0E-01	-	-
Fluoranthene	μg/l	300	< 1.0E-01	< 1.0E-01	< 1.0E-01		
Fluorene	μg/l	300	8.0E-01	4.0E-01	6.0E-01	3.0E-01	1.1E+00
Naphthalene	μg/l	300	< 1.0E-01	< 1.0E-01	< 1.0E-01	-	-
Phenanthrene	μg/l	100	< 1.0E-01	< 1.0E-01	< 1.0E-01	-	-
Pyrene	μg/l	200	< 1.0E-01	< 1.0E-01	< 1.0E-01	-	-

Well K10 - 1 sample

Chemical	**Unit**	**Drinking water**	**Max**	**Min**	**Mean**	**STDV**	**95% UCL**
Acenaphthene	μg/l	400	4.0E-01	4.0E-01	4.0E-01	-	-
Anthracene	μg/l	2000	< 1.0E-01	< 1.0E-01	< 1.0E-01	-	-
Benzo(a)pyrene	μg/l	0.005	< 1.0E-01	< 1.0E-01	< 1.0E-01	-	-
Chrysene	μg/l	5	< 1.0E-01	< 1.0E-01	< 1.0E-01	-	-
Fluoranthene	μg/l	300	< 1.0E-01	< 1.0E-01	< 1.0E-01	-	-
Fluorene	μg/l	300	< 1.0E-01	< 1.0E-01	< 1.0E-01	-	-
Naphthalene	μg/l	300	< 1.0E-01	< 1.0E-01	< 1.0E-01	-	-
Phenanthrene	μg/l	100	< 1.0E-01	< 1.0E-01	< 1.0E-01	-	-
Pyrene	μg/l	200	< 1.0E-01	< 1.0E-01	< 1.0E-01	-	-

5.2.2 Summary of the GrundRisk simulations

The GrundRisk results can be summarized in two parts. Firstly, the GrundRisk results showed that the benzo(a)pyrene and chrysene concentrations (the latter for only well 31R) are above the groundwater acceptable levels for drinking (see Figure 5.5 & 5.6 and Table 5.9). Therefore, based on these results and considerations, the human health risk assessment should give significant health risks for only these two PAH compounds because they exceed the groundwater guidelines for potable water.

Secondly, the analysis on the concentrations detected by the wells of the POVET database, located in the main groundwater flow path (see Figure 5.7), showed that the situation before the water intake plant seems to be under secure conditions, i.e. the concentrations are below the groundwater guidelines (see Table 5.11). Therefore, the human health risk assessment on the concentrations detected in the wells located along this path was considered not relevant. Further considerations about the limitations of the GrundRisk model are discussed in Chapter 6.2.

5.3 Human health risks

This section shows the results of the human health risk assessment executed on the two groups of contaminants. Due the similarities between the default values for the male and the female group (see Table 6 and 7 in Appendix 4), it was decided to make the calculations for only the males. The section is divide into three parts: the results for the chlorophenols, for the polycyclic aromatic hydrocarbons and a summary with the key results of the calculations.

5.3.1 Risks of exposure to Chlorophenols

The human health risk assessment on the chlorophenols (CPs) was based on the concentrations detected in the wells installed by the Finnish Consulting Group. In order to calculate the highest Hazard Quotients for these chemicals, the maximum concentration in groundwater detected in these wells was considered for the calculations (fourth column of Table 4.3).

It was assumed that adults and children drink respectively 2 and 1 L of water per day (see Chapter 4.5). Calculations were done according to Equation 4.15 by taking into account different exposure factors EFs (see Equation 4.14). Table 5.12 shows the results regarding the ingestion exposures for a daily exposure (EF = 1, i.e. an exposure for every day of the year), which were compared to the reference doses RfDs (see Table 4.7). Table 8 in Appendix 4 shows the ingestion doses for a frequency of exposure F equal to 30 (EF = 0.08), 104 (EF = 0.28) and 208 days (EF = 0.57). The frequency of exposure was chosen in order to get a general idea on how the dose changes according to the exposure of human beings to the contaminants. To avoid obtaining similar results between the groups of age, the ingestion exposure was only calculated for one group of children, i.e. between 6 and 11 years old. By looking at the results reported in Table 5.12 and 8 in Appendix 4, for EF = 0.08, 2-CP, 2,4-DCP and 2,4,6-TCP never exceed the reference doses RfDs. By increasing the frequency of exposure, the ingestion doses increase until, for a daily exposure, all the compounds, in particular 2,3,4,6-TeCP, exceed the ingestion reference dose $RfD_{Ingestion}$ (in exception of 2,4,6-TCP for adults and children). According to this model, due to the low body weight, the infant group is the one with the highest doses calculated.

Table 5.12: Males, exposure dose D from ingestion, for a daily exposure (EF = 1), of water containing Chlorophenols (CPs). The value is highlighted in red if it is above the reference dose RfD

Males, ingestion exposure D [mg/kg/day] for a daily exposure (EF = 1)

Chemical	$RfD_{Ingestion}$ [mg/kg/day]	D, infant (6 < 12 months)	D, child (6 < 11 years)	D, adult (> 21 years)
2-CP	5.0E-03	4.2E-02	1.2E-02	9.1E-03
2,4-DCP	3.0E-03	3.1E-02	9.0E-03	6.7E-03
2,3,4,6-TeCP	3.0E-02	1.1E+01	3.1E+00	2.3E+00
PCP	5.0E-03	2.5E-01	7.5E-02	5.6E-02

The dermal exposure was calculated according to Equation 4.16. The parameters used for these calculations are reported in Table 4.8, 6 and 7 in Appendix 4. The results are showed in Figure 5.8. The task considered the same groups of age used for calculating the ingestion exposures. The exposure time ET for a shower/bathing was assumed equal to 20 and 12 minutes for respectively children and adults. The exposure factor EF was assumed equal to 1 for a daily exposure (i.e. a shower taken every day of the year). It was not possible to determine the intake through dermal exposure for 2,3,4,6-TeCP because the dermal permeability coefficient P could not be found for this chemical (see Table 4.8). As it can be seen from Figure 5.8, for EF equal to 1, only pentachlorophenol exceeds the dermal reference dose RfD_{Dermal}.

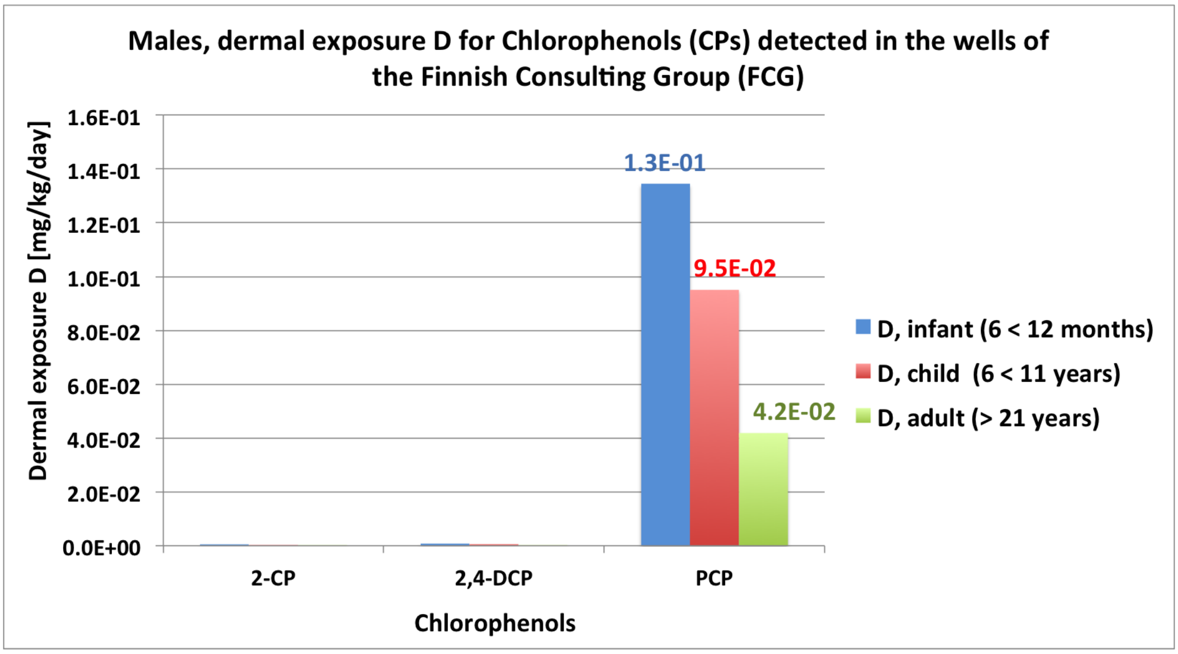


Figure 5.8: Males, exposure dose D from dermal contact, for a daily exposure (EF = 1), with water containingf Chlorophenols (CPs). The value is colored if it is above the reference dose RfD

Figure 5.9 shows the results of the Hazard Index HI (see Equation 4.19), which is given by the sum of the Hazard Quotients HQs of each chemical in a specific exposure route (see Equation 4.18). Further details about the HQ and the HI can be found in Table 10 and 11 in Appendix 4. All the results are above the acceptable level of 1 (for non-carcinogenic risks).

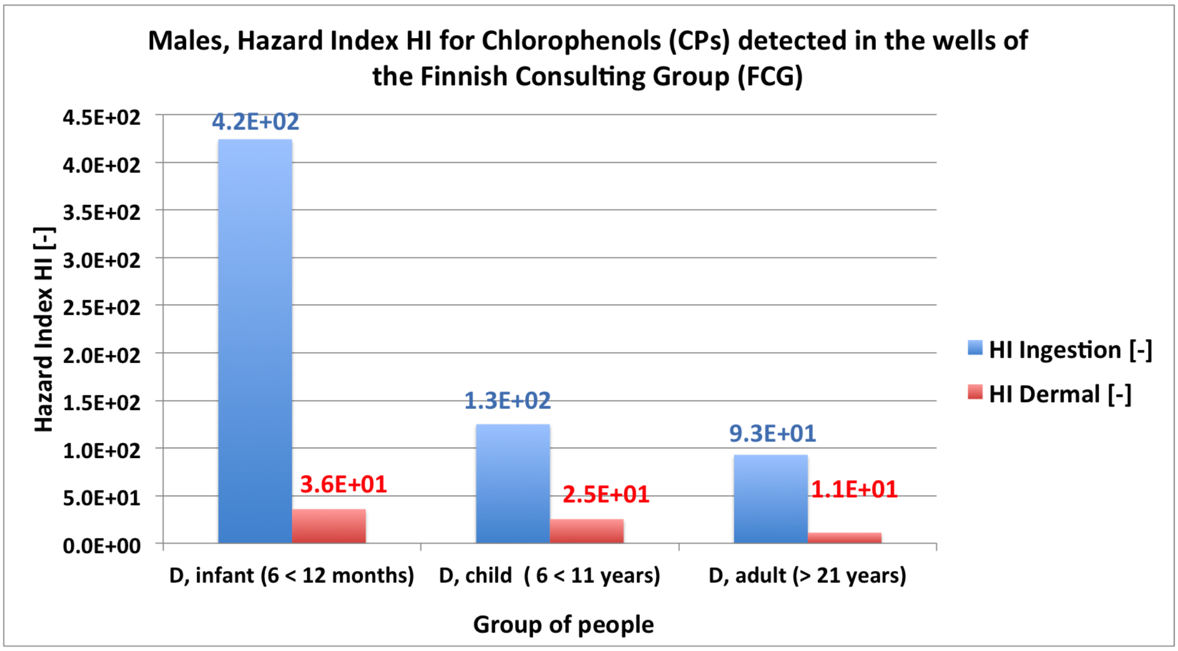


Figure 5.9: Males, Hazard Index HI given by the sum of the intakes of each Chlorophenol (CP) for a daily ingestion exposure and a daily dermal contact (EF = 1). The value is colored if it is above the acceptable level of 1

Table 5.13 shows the cumulative Hazard Index HI (see Equation 4.20), which gives the total non-carcinogenic risk for each chemical in the three groups of people. According to this analysis, the highest Hazard Index belongs to the group of infants.

Table 5.13: Cumulative Hazard Index HI considering the ingestion and dermal exposure route for Chlorophenols (CPs). The value is colored if it is above the acceptable level of 1

Group of people	**Cumulative HI [-]**
D, infant (6 < 12 months)	4.6E+02
D, child (6 < 11 years)	1.5E+02
D, adult (> 21 years)	1.0E+02

5.3.2 Risks of exposure to Polycyclic Aromatic Hydrocarbons

The procedure used for the CPs were repeated for the polycyclic aromatic hydrocarbons (PAHs). The concentrations used for this analysis were taken from the results of the GrundRisk simulations (see Table 5.9). Firstly, it was decided to present the calculations of the Hazard Quotients for the well, which, according to the GrundRisk simulations, had the maximum concentrations in the groundwater of Pursiala. By looking at the GrundRisk results in Table 5.9, the maximum concentration in the groundwater was obtained (with GrundRisks) in well 31R. Results for a daily ingestion exposure (see Equation 4.15) are presented in Figure 5.10. Further details about these results are available in Table 12 and 13 in Appendix 4. For all the contaminants, the doses calculated are always below the ingestion reference dose $\mathrm{RfD}_{Ingestion}$.

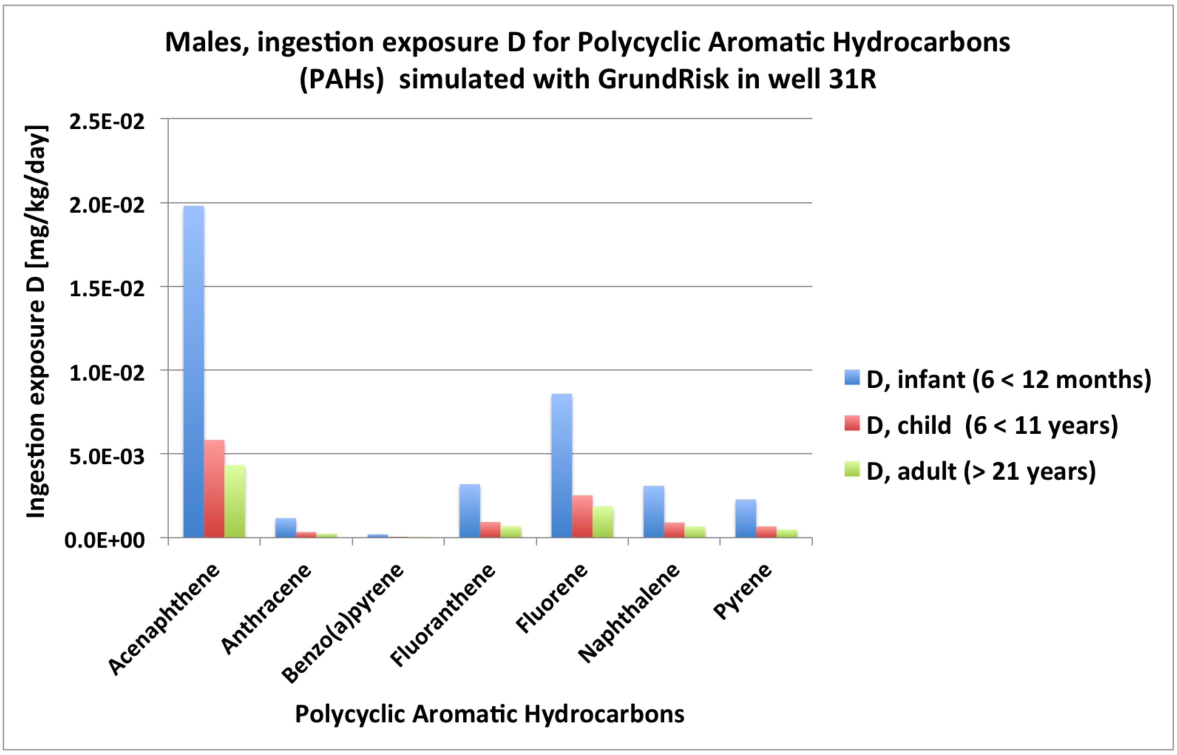


Figure 5.10: Males, exposure dose D from ingestion, for a daily exposure (EF = 1), of water containing Polycyclic Aromatic Hydrocarbons (PAHs), simulated with GrundRisk, detected in well 31R. All the values are below the reference dose RfD

The analysis continued by determining the dermal exposures (see Equation 4.16). The results are available for only benzo(a)pyrene, chrysene, fluoranthene, naphthalene and phenanthrene because the dermal permeability coefficient P was not found for the other PAH compounds (see Table 4.8). As it can be seen in Figure 5.11, for a shower taken every day of the year (exposure factor EF=1, i.e. a daily exposure), no chemical exceeds the dermal reference dose RfD_{Dermal}. Further details about these results can be found in Table 14 in Appendix 4.

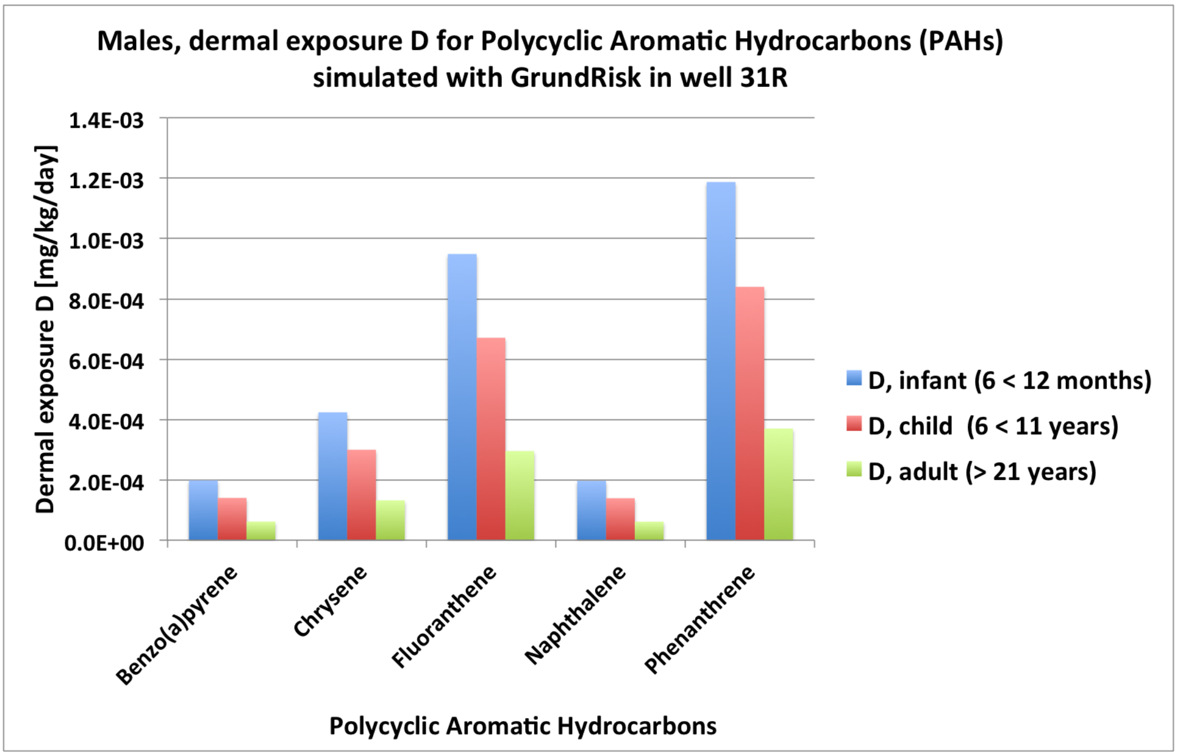


Figure 5.11: Males, exposure dose D from dermal contact, for a daily exposure (EF = 1), with water containing Polycyclic Aromatic Hydrocarbons (PAHs), simulated with GrundRisk, detected in well 31R. All the values are below the reference dose RfD

Figure 5.12 shows the results of the Hazard Indexes HIs (see Equation 4.19). The infant is the only group where the HI is above the acceptable level of 1. The complete results for the Hazard Quotients HQs and the HIs can be found in Table 15 and 16 in Appendix 4. The analysis proceeded with the calculation of the cumulative Hazard Indexes (see Equation 4.20). As Table 5.14 shows, the highest cumulative HI was found for the group of infants.

Table 5.14: Cumulative Hazard Index HI considering the ingestion and dermal exposure route for Polycyclic Aromatic Hydrocarbons (PAHs) detected in well 31R. The value is highlighted in red if it is above the acceptable level of 1

Group of people	**Cumulative HI** [-]
D, infant ($6 < 12$ **months**)	2.3
D, child ($6 < 11$ **years**)	1.0
D, adult (> 21 **years**)	0.6

At the point of compliance (POC), i.e. well 50R (see Figure 5.4), the groundwater guidelines are only exceeded by benzo(a)pyrene. Calculations executed on the intakes through ingestion and dermal path showed values below the reference doses RfDs (see Table 17 and 18 in Appendix 4).

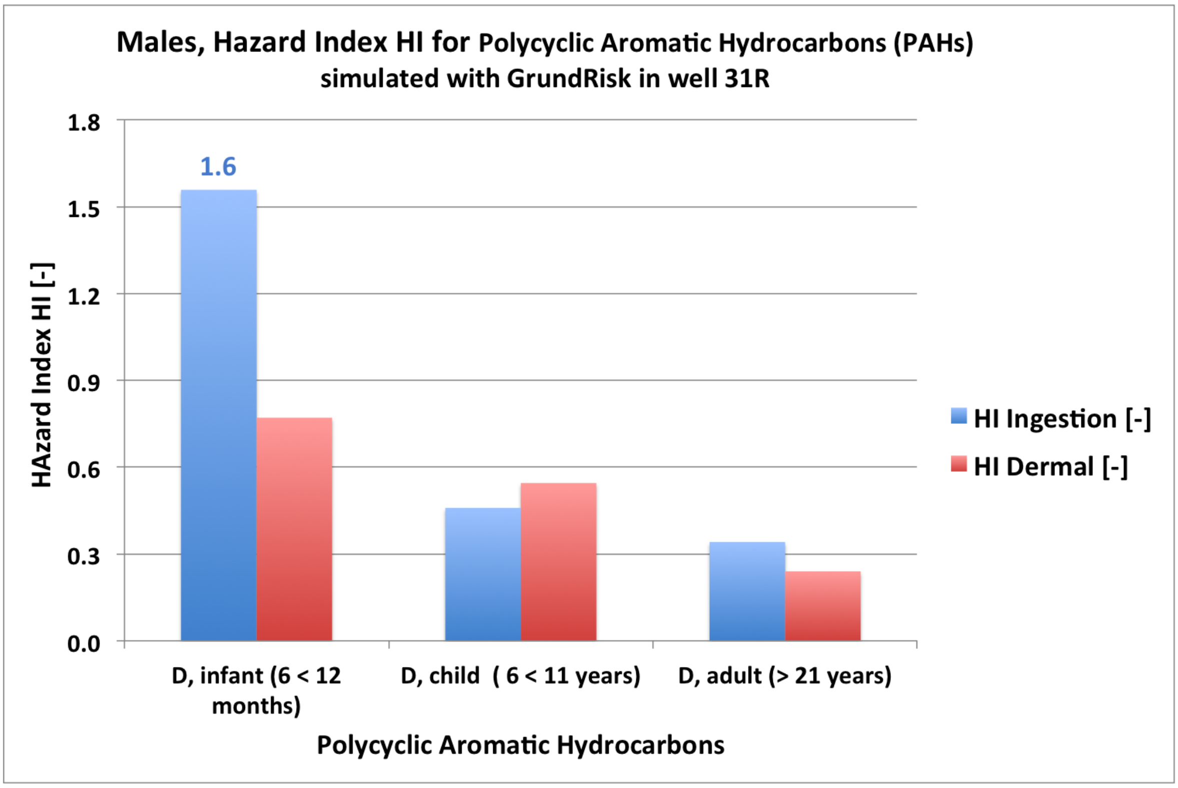


Figure 5.12: Males, Hazard Index HI given by the sum of the intakes of each Polycyclic Aromatic Hydrocarbon (PAH), detected in well 31R, for a daily ingestion exposure and a daily dermal contact (EF = 1). The value is colored it is above the acceptable level of 1

The calculations of the Hazard Index were all below the acceptable level of one (see Table 19 and 20 in Appendix 4). Consequently, as Table 5.15 shows, there is no significant risk to human beings at the point of compliance because, according to these calculations, all the cumulative Hazard Indexes are below the acceptable level of 1.

Table 5.15: Cumulative Hazard Index HI considering the ingestion and dermal exposure route for Polycyclic Aromatic Hydrocarbons (PAHs) detected in well 50R

Group of people	**Cumulative HI [-]**
D, infant (6 < 12 months)	2.0E-01
D, child (6 < 11 years)	1.0E-01
D, adult (> 21 years)	6.0E-01

An additional analysis on the PAHs was executed by considering the concentrations measured in the source area in the aquifer around the wood impregnation plant (see Table 4.2). As before, only the results of the Hazard Indexes HIs are showed. Details for the intakes through a daily ingestion and daily dermal exposure can be found in Table 21 and 22 in Appendix 4. The results reported in Figure 5.13 show that, in comparison to the previous results (see Figure 5.12), acenaphthene, benzo(a)pyrene, fluoranthene, fluorene, naphthalene and pyrene represent a non-carcinogenic risk for the local people of the area (especially for infants). Details of the Hazard Quotients and Indexes are showed in Table 23 and 24 in Appendix 4.

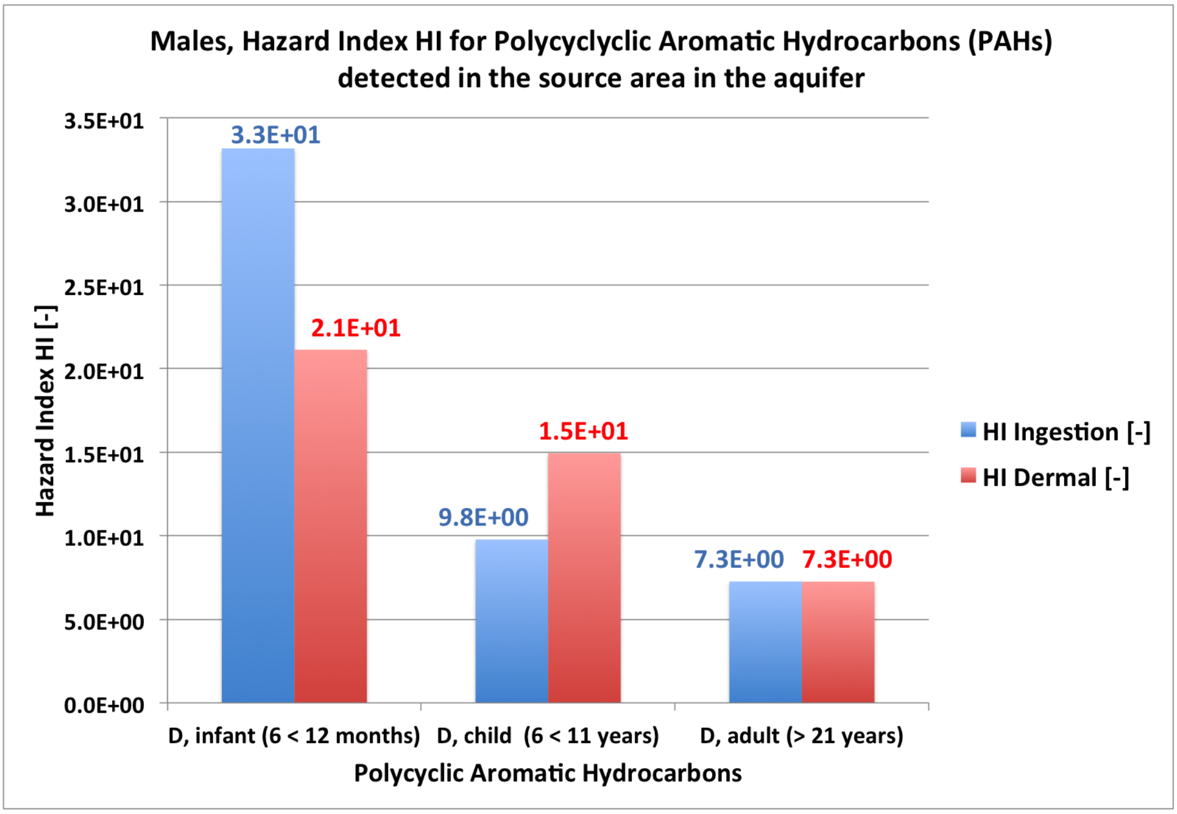


Figure 5.13: Males, Hazard Index HI given by the sum of the intakes of each Polycyclic Aromatic Hydrocarbon (PAH), detected in the source area in the aquifer, for a daily ingestion exposure and a daily dermal contact (EF = 1). The value is colored it is above the acceptable level of 1

Lastly, the cumulative Hazard Index HI was calculated by summing the Hazard Indexes for the ingestion and the dermal exposure route. As Table 5.16 shows, the highest HI was calculated for the infants.

Table 5.16: Cumulative Hazard Index HI considering the ingestion and dermal exposure route for Polycyclic Aromatic Hydrocarbons (PAHs) detected in the source in the aquifer. The value is highlighted in red if it is above the acceptable level of 1

Group of people	**Cumulative HI [-]**
D, infant (6 < 12 months)	5.4E+01
D, child (6 < 11 years)	2.5E+01
D, adult (> 21 years)	1.4E+01

5.3.3 Summary of the human health risks

Figure 5.14 visualizes the highest cumulative Hazard Indexes HI calculated in the three case. The analysis on the CP concentrations detected in the aquifer by the Finnish Consulting Group (see Chapter 5.3.1), on the PAH concentrations obtained by the GrundRisk simulations at the point of compliance and on the PAH concentrations detected in the source area in the aquifer (see Chapter 5.3.2). According to the comparison with the reference doses RfDs and the level of 1 for the Hazard Quotient/Index, the areas around the wood impregnation plant and the sawmill represent (especially the latter) a significant health risk to human beings. In addition, the group of infants is the one, according to these calculations, always having the highest Hazard Quotient/Index.

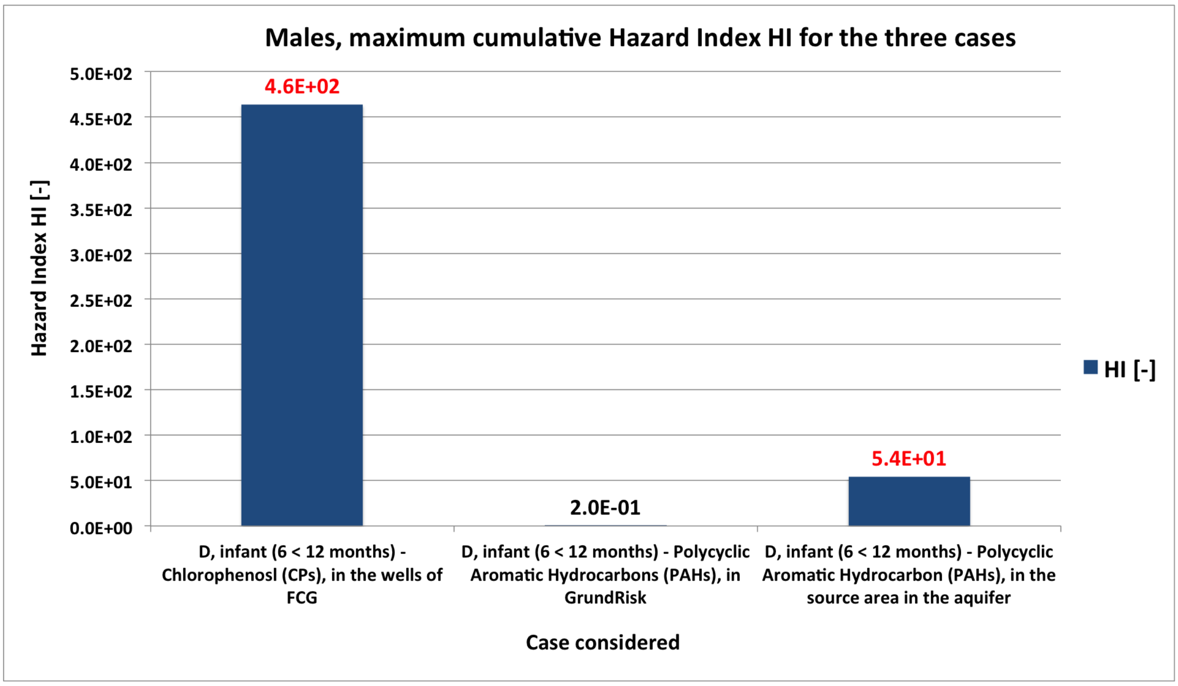


Figure 5.14: Maximum Hazard Index HI for three cases considered. The value is highlighted in red if it is above the acceptable level of 1

6. Discussion

The analysis in the Master's Thesis was developed by applying the DRASTIC method, which gave as result a high vulnerability of the aquifer. Moreover, the GrundRisk tool modeled the dispersion of the contaminants in the area around the wood impregnation plant at a point of compliance (POC) set at 500 m from the source area in the aquifer (see Figure 5.4). The simulation gave benzo(a)pyrene and chrysene concentrations above the groundwater guidelines (see Figure 5.5 & 5.6 and Table 3 in Appendix 2). Lastly, a human health risk assessment was executed. The method gave HQ/HI values above the acceptable level of 1, especially for the area around the sawmill (see Figure 5.14). Therefore, it could be stated that the industrial activities in Mikkeli cause significant health risks for the local people. The conclusions derived from a series of approximations and uncertainties (especially in the GrundRisk simulations) that have to be taken into account in order to understand the reliability of the results. This chapter is divided into four sections: the first three discuss the reliability and the uncertainties of the models used in the Master's Thesis, with a comparison between the other tools described in Chapter 2. The comparison with groundwater models was challenging not only because of the large number of softwares that can be used for modelling groundwater phenomena and that could have been therefore chosen for a comparison, but even because it was hard to find scientific articles discussing this topic in Finland. Consequently, the comparison with the other models was focused on their outputs and procedures. The last section presents the main outcomes of the Master's Thesis.

6.1 Aquifer vulnerability

Due to the similar hydrogeological characteristics, the area around the wood impregnation plant and the sawmill have an analogous DVI index. Consequently, the considerations drawn from them are similar. The only relevant difference between the two cases is the depth to the water table D (see Table 3.1), which, in the the area around the sawmill, has a lower depth and makes the aquifer more vulnerable than in the area around the wood impregnation plant. The lower is D, the easier is for the contaminant to reach the groundwater. The DRASTIC analysis gave as a result a high degree of vulnerability for the two areas: detailed site investigations, including ongoing monitoring and protection design factors should be executed [105]. As it can be seen from Table 5.1 and 5.5, there is more than one hydrogeological parameter having different ratings in the two areas. Multiple combinations of these parameters might have brought to different DVI indexes, but it would not have added useful information for the purpose of the Master's Thesis, which aimed to obtain a range for the vulnerability of the aquifer.

No particular difference was found between the procedure adopted in the Master's Thesis and in the scientific articles reported in Chapter 2.1. DRASTIC is a very simple tool, and it is not surprising to find similar procedures in diverse works (the considerations obtained is, of course, what makes them different). The map removal sensitivity analysis (see Equation 4.3), elaborated by Lodwick et al. [35], was conducted to understand if all the parameters were necessary for determining the vulnerability of the aquifer [36]. The analysis showed that not all the seven parameters were significant. Therefore, some of them (e.g. the topography T) can be excluded from the DVI index because their removal does not causes an incorrect interpretation of the vulnerability of the aquifer. The single parameter sensitivity analysis (see Equation 4.4), elaborated by Napolitano et Fabbri [36], was executed to compare the "real" weight of the parameters to the one assigned by the DRASTIC method. The vulnerability of the two areas slightly increased due to the calculation of the new weights of the parameters. As a consequence, the influence of the geological characteristics on the vulnerability of the Pursiala aquifer became clearer. In fact, nevertheless the initial weight of the depth to the water table D, which makes it, together with the the impact of the soil type of the vadose zone I, the parameter mostly affecting the vulnerability in an aquifer (see Table 4.4), the sensitivity analysis revealed that D is not a very important parameter for the vulnerability of the aquifer. This result is not surprising considering that the depth to the water table is quite high (especially for the PAH case). In addition, the net recharge R became the parameter mostly influencing the vulnerability. The other parameters did not have any significant change. In conclusion of the sensitivity analysis, the net recharge R, the aquifer soil type A and the impact of the soil type of the vadose zone I revealed to be the parameters influencing most the vulnerability of the aquifer (see Table 5.4 and 5.8). The study of R can be very complicated because the parameter is directly related to seasonal factors and to the soil characteristics (e.g. the vegetation influences the quantity of water that evaporates and infiltrates in the soil). Groundwater is recharged naturally by rain, but its measurement and prediction are very difficult because rainfall varies in time and space [106]. In addition, it is very difficult to quantify the processes in the vadose zone and to check if the contamination represents a threat to the groundwater [107] [108]. When dealing with a contamination problem in deep vadose zones (normally down 18 m), it is hard to obtain information on them because they are below the zone of practical excavation [109].

The DRASTIC method is the American version of SINTACS and have only small differences. By giving an example, the weight of the soil type layer S is 2 and 4 for, respectively, the DRASTIC and the SINTACS method. By comparing the procedures adopted in this Master's Thesis and the one by Kumar with SINTACS [37], they are, as expected, very similar. The difference is that, in the study by Kumar, the tool was used together with geo-referential tools, which is quite common when using this method (e.g. the study by Gutpa [33]). In addition, the vulnerability of the aquifer was assessed by comparing the SINTACS indexes, calculated in each part of the aquifer, with the chemical concentrations detected in the aquifer [28]. These operations were not executed in the Master's Thesis. The lack of geo-referential data for Pursiala prevented to represent the aquifer in tools like ArcGIS and to visualize the variation of the vulnerability in the aquifer. The comparison between the field data (i.e. the concentrations detected in the aquifer) and the DVI indexes was not considered relevant because this operation is normally executed when dealing with high variations of the DVI index, i.e. when dealing with (normally) big areas. In comparison to the Kumar case, which considered an area of 764 km^2 [28], the two areas analyzed in the Master's Thesis are much smaller, i.e. 0.2 and 0.1 km^2 for respectively the sawmill and the wood impregnation plants. Therefore, each hydrogeological parameter either has a very small range or keeps the same value in every part of the area. This explains why it was not necessary to make a division of the two areas in small sub-areas, and calculate the DVI index for each of them: they are so small that a detailed knowledge on the variation of the hydrogeological parameters would have (probably) not caused any significant variation of the vulnerability index. On the other hand, if the DRASTIC analysis had been conducted on the whole Pursiala aquifer, which has an area of 4.3 km^2, the division of the aquifer in sub-areas and a comparison between the indexes and the field data would have been necessary for a correct analysis with DRASTIC.

DRASTIC does not represent a scientific method for predicting the contamination because the results do not imply the occurrence of the contamination in the area [110]. This explains why other procedures need to be applied to describe the behavior of the contaminants in the aquifer (e.g. modelling tools). Despite that, the DRASTIC method is largely used worldwide (and in Finland) because of the accuracy of the details given by the tool. Many studies on the vulnerability were successfully conducted with the DRASTIC method, and the Master's Thesis confirmed this trend: it is an excellent and cheap way to determine the vulnerability of the aquifer and it is very useful in determining groundwater strategies and managing aquifers' protection.

6.2 Modelling tool

Between the groundwater tools described in Chapter 2.2, GrundRisk was the most suitable for this project. The study conducted by Artimo et al. [37] and Purjenaie et al. [39] proved that the outputs of MODFLOW are very different in comparison to GrundRisk. While the latter aims only to model the contaminants' dispersion in an aquifer, the formers have several applications, which allow determining, for example, the hydrogeological distribution in the aquifer. The modelling of the contaminants' dispersion in the aquifer is possible in MODFLOW, as described in the study by Saghravani & Mustapha [41] and by Artimo [40], who simulated the dispersion of the contaminants in the aquifer trough softwares associated to MODFLOW. All the studies cited, in comparison to GrundRisk, are more complex because they require a high detailed information on the aquifer to work correctly (e.g. bedrock properties or hydraulic head values). This is the reason for why GrundRisk was chosen for the Master's Thesis because it allowed obtaining the distribution of the contaminants in the aquifer without acquiring all those detailed information of the area. The choice of this modelling tool was supported by some Danish case studies [92] where GrundRisk was applied to show the performance of the model in contaminated sites. No comparison is shown in the Master's Thesis with these previous studies because none of them considered the same situation of model number V. A comparison between the results obtained with GrundRisk and Bioscreen was not executed because Bioscreen is set for describing the natural attenuation of BTEX compounds. It would have been difficult to use the software for other chemicals because the input parameters of Bioscreen should have been modified and adapted to the chemicals of interest and to the study area [42]. In addition, it would have been complicated to simulate the biodegradation in Bioscreen because there was no information available about the electron acceptors in the site. Lastly, GrundRisk is more precise to model the variation of the contaminants along the aquifer, while Bioscreen aims at describing if their natural attenuation may happen at a reasonable time, which was not of interest in this project.

The GrundRisk simulations were executed considering a high number of assumptions (see Chapter 4.4). In addition, model number V considers a direct input from the contaminant source on top of the aquifer (see Figure 4.5), while in the real case, i.e. Mikkeli, there is no contamination in the soil above groundwater anymore because the soil has been remediated. The contaminants are only in groundwater, below it and in the soil-bedrock interface. Like all the GrundRisk models, model number V does not really describe this situation since it assumes there is still a source of contamination. This difference was considered acceptable for the Master's Thesis. The simulations were only run in the area contaminated by the PAH compounds but, because of the limitations of GrundRisk (see Chapter 4.4), they were only executed in the path next to the plant itself, i.e. between the wood impregnation plant and well 50R (500 m). In this path, GrundRisk simulated concentrations above the groundwater guidelines for benzo(a)pyrene and chrysene (see Table 5.9). Even if the concentration of the single chemical is below the groundwater guideline, the mixture of the chemicals might bring to a concentration exceeding the groundwater guideline. This aspect could not be considered in the Master's Thesis because GrundRisk does not consider any joint toxic action due to the presence of multiple chemicals in the aquifer. No simulation was run in the main groundwater flow path, i.e. in the direction of the water intake plant (see Figure 5.7). The analysis in this path was conducted through the study of the concentrations detected in the wells of the POVET database (see Table 5.11). In this path, due to several phenomena like dilution, the analysis of the wells of the POVET database gave concentrations below the groundwater guidelines. In the sawmill area, the results of the simulations are missing because of the lack of concentrations in the source area. Considering its vicinity to the water intake plant, the GrundRisk analysis would have been very interesting, but problems would have arisen considering the pumping stations in the area, which drastically alter the groundwater level, flow and volume of the area (see Figure 4.1). These situations can complicate the possibility to model the dispersion of the contaminants in the aquifer not only in GrundRisk, but even in other modelling tools. By giving an example, Bioscreen cannot be applied under these conditions because the model gives only reasonable results in area where pumping systems do not create a complicated flow field [42]. It was only by analyzing the concentrations of the wells installed by FCG (see Table 4.3) that it was possible to state that the CP concentrations are above the groundwater guidelines.

GrundRisk was calibrated in order to obtain similar concentrations detected in the groundwater observation wells of the POVET database (see Table 3 in Appendix 2). This is not how GrundRisk normally works because it is usually not calibrated. GrundRisk is in fact used in such an early stage of studies to only give an idea about the contaminants' dispersion in the aquifer. The calibration was executed in the Master's Thesis because the goal was to examine if this modelling tool is applicable to the Finnish conditions (see Chapter 2.2). The first order degradation rate λ was the parameter influencing most the GrundRisk simulations. The calibration was executed according to this parameter. It was inserted in the model due to evidences of the chemical degradation in the aquifer. Because no exact information could be collected about the degradation in the area around the wood impregnation plant, the study conducted by Howard et al. [96] on the chemical degradation, which was cited in many scientific articles, was chosen as a reference. As it can be seen from the POVET database (see

Table 3 in Appendix 2), apart from the naphthalene concentrations in well 35R, the concentrations are always below the guideline values. In addition, the concentrations are characterized by high variations, which are quite normal in every sampling operations. The samples were taken at different depths and times (precisely from 2009 to 2011 for well 31R, 2011 for 35R and 42R and 2010 for 50R), at different weather and seasonal conditions. By giving an example, the naphthalene concentration measured in 2010 at 74.90 m in well 50R was of 0.5 μg/l, while the concentration in well 42R measured at 75.00 m (in the same year) was of 130 μg/l. GrundRisk was calibrated in order to obtain concentrations that were actually measured in the POVET wells around the wood impregnation plant (see Chapter 4.4). As every model, GrundRisk was not expected to give exact values and the calibration was not expected to be perfect. The simulations run in GrundRisk were 30. Table 6.1 shows how many times, considering 30 simulations for each chemical, it was possible to obtain GrundRisk results that were consistent with the concentrations detected in the wells of the POVET database (see Table 3).

Table 6.1: Number of GrundRisk simulations consistent with the concentration range in the POVET database

		Well			
		31R [μg/l]	**35R** [μg/l]	**42R** [μg/l]	**50R** [μg/l]
Acenapthene	POVET range (maximum and minimum concentration detected in the POVET well)	0.10 - 0.47	100 - 350	210 - 300	0.13 - 0.61
	Number of GrundRisk simulations consistent with the concentration range in POVET	**0**	**0**	**0**	**6**
Anthracene	POVET range (maximum and minimum concentration detected in the POVET well)	< 0.1	0.74 - 2.60	0.85 - 1.00	< 0.1
	Number of GrundRisk simulations consistent with the concentration range in POVET	**0**	**18**	**0**	**1**
Benzo(a)pyrene	POVET range (maximum and minimum concentration detected in the POVET well)	< 0.1	< 0.1	< 0.1	< 0.1
	Number of GrundRisk simulations consistent with the concentration range in POVET	**0**	**0**	**22**	**26**
Chrysene	POVET range (maximum and minimum concentration detected in the POVET well)	< 0.1	< 0.1	< 0.1	< 0.1
	Number of GrundRisk simulations consistent with the concentration range in POVET	**0**	**0**	**1**	**2**
Fluoranthene	POVET range (maximum and minimum concentration detected in the POVET well)	< 0.1	0.29 - 2.10	< 0.1	< 0.1
	Number of GrundRisk simulations consistent with the concentration range in POVET	**0**	**5**	**0**	**0**
Fluorene	POVET range (maximum and minimum concentration detected in the POVET well)	0.11 - 0.17	38 - 100	73 - 100	0.1 - 0.2
	Number of GrundRisk simulations consistent with the concentration range in POVET	**0**	**0**	**0**	**7**
Napthalene	POVET range (maximum and minimum concentration detected in the POVET well)	0.20 - 1.30	69 - 970	110 - 220	0.1 - 0.5
	Number of GrundRisk simulations consistent with the concentration range in POVET	**0**	**0**	**0**	**5**
Phenanthrene	POVET range (maximum and minimum concentration detected in the POVET well)	0.1 - 0.3	11.0 - 43.0	42.0 - 36.0	< 0.1
	Number of GrundRisk simulations consistent with the concentration range in POVET	**0**	**20**	**0**	**0**
Pyrene	POVET range (maximum and minimum concentration detected in the POVET well)	< 0.1	0.11 - 0.81	< 0.1	< 0.1
	Number of GrundRisk simulations consistent with the concentration range in POVET	**0**	**16**	**0**	**7**

The highest number of consistencies between the GrundRisk results and the range of the chemicals in the POVET database (59) belongs to well 35R. Well 50R is the one that was best modeled by GrundRisk because the consistencies between the modelling tool and the range of the POVET database were not found for only two chemicals (i.e.

fluoranthene and phenanthrene). No consistency for well 31R was ever found between GrundRisk and POVET. In addition, according to these simulations, benzo(a)pyrene and chrysene were the chemicals that, respectively, had the highest and the lowest number of consistencies with the range of the POVET database.

According to Table 6.1, some similarities were found between the GrundRisk results and the concentrations detected in the wells of the POVET database. In conclusion, it can be stated that the model can describe correctly the dispersion of the contaminants in an aquifer and that it can be used for future groundwater applications. Despite some differences with the POVET database, it is not possible to say that the model is not reliable just for these differences because the simulations were done under many uncertainties and approximations (see Chapter 4.4). In addition, as it was mentioned early, GrundRisk is a very simple risk assessment tool, and it was never expected to simulate the exact concentrations detected in the aquifer.

6.3 Human health risk assessment

The results obtained from the GrundRisk simulations, and the concentrations compiled by the Finnish Consulting Group, highlighted the necessity to conduct a human health risk assessment on these two groups of chemicals. The calculation of the Hazard Quotients/Indexes is the most typical approach used in the case of human exposure to contaminants in the environment. This explains why there is not much literature about other methods in the Master's Thesis. The human health risk assessment was elaborated by considering default values by EPA. No analysis was executed on the cancer risks. They are normally calculated by considering a carcinogenic slope factor of each chemical. This parameter is not available in the IRIS database for most of the chemicals considered in this Master's Thesis. To be precise, the slope factor is available only for 2,4,6-trichlorophenol, pentachlorophenol, benzo(a)pyrene and chrysene. Therefore, due to this limited information, it was decided to make no calculation of the cancer risks. Their calculations would have not changed the conclusions because the risks in the area were already stated by the calculations of the Hazard Quotients/Indexes, but it would have given additional information about the health risks.

The highest values of the HQs/HIs were calculated for the groups of infants (see Figure 5.14). According to this analysis, they were the most vulnerable target group to a contamination exposure. The results for the children were proposed for only one group, while all the adults were put together in one single group (i.e. people with an age higher than 21). In addition, the inhalation exposure was assumed to be not important for this Master's Thesis (see Chapter 4.5). The results showed in Chapter 5.3 proved that the risk for human beings could be assessed even without calculating the doses through inhalation exposure. These choices did not affect the reliability of the human health risk assessment but only its degree of detail, which is not a problem considering that the main focus of the project was the groundwater risk assessment of the Pursiala aquifer. Due to the many studies conducted on these chemicals, which proved health risks related to the exposure of them (see Chapter 3.2), it was important to conclude the Master's Thesis by quantifying the risks for people living in the area around the Pursiala aquifer. The risk assessment might be repeated on the females group. Due to their exposure that can result in the exposure of the unborn child, females are normally considered as a sensitive group rather than males. The results for the females should not be so different from the ones obtained in this Master's Thesis because, as Table 6 and 7 in Appendix 4 show, there is no such big difference between the default parameters of males and females. It should be said that, even if no reference dose could be found for some of the PAHs and CPs, they might also have potential adverse effects on local residents. In addition, even if some concentrations were found below the acceptable level, there may be joint toxic actions which bring to an excess of the acceptable levels.

The Hazard Quotients/Indexes calculated for the CPs in the area around the sawmill were all above the acceptable level of 1 (Table 10 and 11 in Appendix 4). The calculations were executed on the maximum concentrations detected for each compound between the wells (Table 1 in Appendix 4). The lack of information on the dermal permeability coefficient for 2,3,4,6-tetrachlorophenol did not compromise the analysis because the health risk of this compound could be estimated thanks to the intakes through ingestion exposure. All the CP concentrations detected in the wells around the sawmill area were above the groundwater guidelines (see Table 4.3).

The analysis on the PAHs was longer due the large amount of data used for the analysis. The Hazard Quotients HQs were not calculated for the PAH concentrations detected by the wells of the POVET database (see Table 3 in Appendix 4) because they were not considered relevant for the analysis. The risk assessment was in fact executed on the GrundRisk results by using the concentrations detected in well 31R, which was the well simulating the highest concentrations from GrundRisk, and well 50R, which was the point of compliance POC (see Figure 5.4). The results of the GrundRisk analysis gave only benzo(a)pyrene and chrysene exceeding the groundwater guidelines. The calculations of the Hazard Quotients/Indexes gave significant health risks fo only benzo(a)pyrene (see Table 19 and 20 in Appendix 4). No significant health risk was found for chrysene because no reference dose could be found for this compound (see Table 4.7). By executing an additional assessment on the concentrations detected in the source area in the aquifer, the calculations gave more than one chemical exceeding the acceptable level of 1 (see Table 23 in Appendix 4). These results are very useful because they describe how the Hazard Quotients, and therefore the risks, vary along the area around the wood impregnation plant. As it can be seen by Figure 6.1, the highest Hazard Index was calculated for the concentrations detected in the source area in the aquifer. At the point of compliance (well 50R) the Hazard Index is below the acceptable level, i.e. no significant health risk for human beings. No human health risk assessment was conducted in the main groundwater flow path because the concentrations detected were below the groundwater guidelines (see Table 5.11).

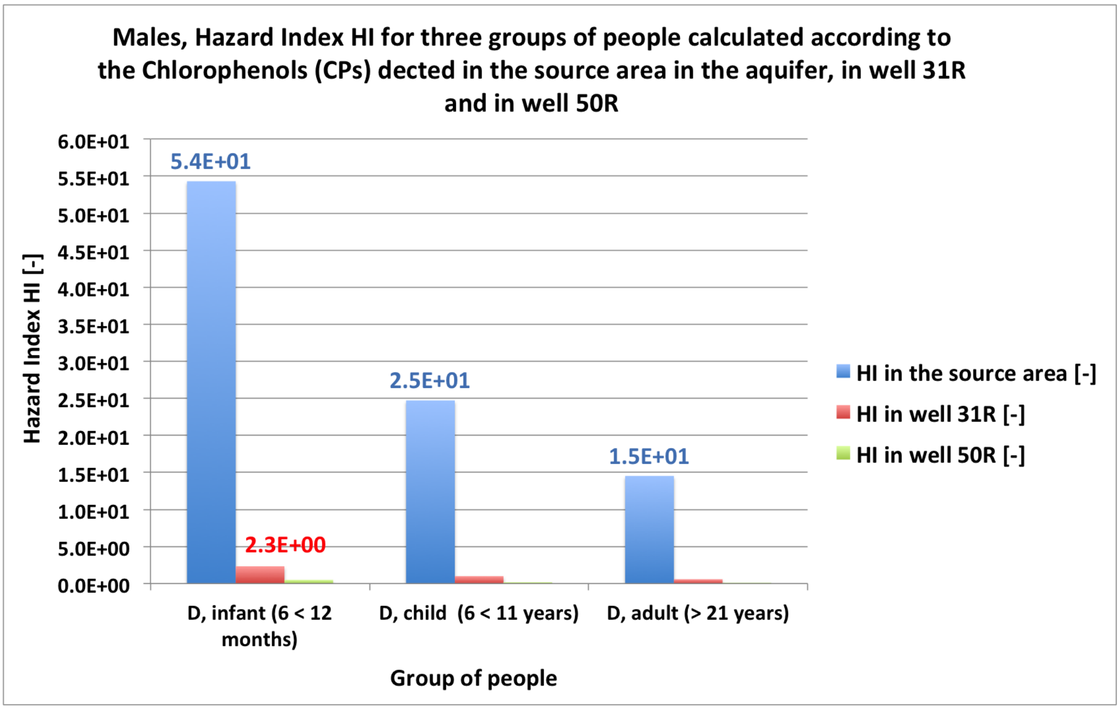


Figure 6.1: Variation of the Hazard Index HI along the path around the wood impregnation plant. The value is colored if it is above the acceptable level of 1

6.4 Summary

The main outcomes of the Master's Thesis procedure can be summarized as it follows:

- the DRASTIC method is very simple, and the analysis was correctly conducted due to the availability of all the hydrogeological parameters of the area;
- the sensitivity analysis related to DRASTIC showed that the key parameters, which strongly influence the vulnerability of the aquifer, are the net recharge R, the impact of the soil type of the vadose zone I and the aquifer soil type A. In addition, the depth to the water table D resulted to be not very relevant for assessing the vulnerability of the aquifer;
- GrundRisk is a preliminary risk assessment tool, i.e. it is not expected to give exact values of the concentrations in an aquifer, but only to give an idea of the contaminants' dispersion in it;
- the consistency of the GrundRisk results with the concentration data in the POVET database proved that the model can be used for future groundwater applications in Finland;
- the human health risk assessment was conducted according to the calculation of the Hazard Quotients/Indexes, which were above the acceptable level of 1. The model gave the highest results and the major risks, respectively, for the infant group and the area around the sawmill.

7. Conclusions

A sawmill and a wood impregnation plant located in the area of the Pursiala aquifer caused a release of chlorophenols and polycylic aromatic hydrocarbons in the groundwater. Conclusions can be drawn thanks to the results discussed in Chapter 5 and 6.

Firstly, an initial analysis on the concentrations detected in the wells of the area, which are collected in the Finnish groundwater database named POVET, showed concentrations above the groundwater guidelines, proving the negative effects of the industrial activities on the groundwater quality. This problem must not be underestimated because the Pursiala groundwater area, as most of the Finnish aquifers, is relied by the population of Mikkeli as a source for potable water.

The vulnerability of the aquifer was analyzed with the DRASTIC method, which revealed a high degree of vulnerability. The sensitivity analysis allowed understanding the impact of each parameter on the DVI and the factors on which the analysis of the area should be mostly focused.

Despite few information available for checking the reliability of GrundRisk, similarities were found between this modelling tool and the POVET database. The model was consistent with the concentrations detected in the wells around the wood impregnation plant. The analysis with this tool can be considered satisfactory, meaning that it is possible to apply this tool in future groundwater applications.

The results in the human health risk assessment confirmed the emergency state in which the Pursiala area finds itself and that the aquifer is not in secure condition. In particular, considering that experiments in many scientific studies proved side effects of these chemicals, people may have serious health problems.

In conclusion, in order to guarantee in the future a higher efficiency of the results and to secure the area, some recommendations can be drawn:

- the study of the vulnerability of the aquifer will be more detailed if geo-referential data are available because it allows representing the area through GIS tools like ArcGIS (something not possible in this thesis), making the comprehension of the problem much easier;

- the availability of hydrogeological parameters for the whole aquifer (the analysis was only conducted in small two areas) will allow to conduct a complete analysis and to present more precise directives for delineating a strategy for the Pursiala risk management;

- GrundRisk can be a useful tool for dealing with the groundwater risk management, but all its simplifications must be clarified in order to understand the reliability of the results. GrundRisk is a very simple software and considers basic characteristics of the aquifer (e.g. homogeneity). It may encounter many problems if applied in heterogeneous soils, which are very common in Finland, or difficult situations (e.g. the one in the sawmill area, which is subjected to many pumping operations);

- more sophisticated tools might be considered in order to produce more detailed risk management decisions, but it is necessary to conduct a more detailed study of the characteristics of the aquifer;
- the carcinogenic effects of the chemicals may be calculated in order to have a more complete vision of the risks for human beings and to increase the degree of detail in the human health risk assessment in Pursiala;
- it is highly recommended to increase the impact of the remediation technologies in the Pursiala area, especially in the one around the sawmill because it is located very close to the water intake plant.

References

[1] McLamb, E. The ecological impact of the industrial revolution, 2011. URL http://www.ecology.com/2011/09/18/ecological-impact-industrial-revolution/. [Cited 19 June 2017].

[2] Sorvari, J. Environmental risk analysis. *Lecture note for WAT-E2150 Environmental Risk Analysis. Department of Built Environment. Aalto University*, 2017. pp. 4-12.

[3] Bengtson, H. Why is groundwater so important?, 2010. URL http://www.brighthub.com/environment/science-environmental/articles/68744.aspx. [Cited 18 June 2017].

[4] Groundwater Foundation. What is groundwater?, 2017. URL http://www.groundwater.org/get-informed/basics/groundwater.html. [Cited 24 July 2017].

[5] Tasmanian Government. Confined and unconfined aquifers, 2016. URL http://dpipwe.tas.gov.au/water/groundwater/aquifers/confined-unconfined-aquifers. [Cited 22 January 2017].

[6] Local Government And Municipal (LGAM) Knowledge Base. Aquifer - LGAM knowledge base, 2017. URL http://www.lgam.info/aquifer. [Cited 26 January 2017].

[7] European Parliament and Council. Directive 2006/118/EC on the protection of groundwater against pollution and deterioration. *Official Journal of the European Union*, 2006. pp. 84-97.

[8] EEA. Groundwater quality and quantity in Europe. *Environmental Assessment Report*, 3:133, 1999. Vol. 3. p. 133.

[9] UNECE. Inventory of transboundary groundwaters. *UNECE Task Force on Monitoring and Assessment. Guidelines on monitoring of transboundary groundwaters, Supporting Technical Documents*, 1991. Vol. 1. p. 281.

[10] Luoma, S. Groundwater vulnerability of a shallow low-lying coastal aquifer in southern Finland under climate change. *GTK*, 2016. pp. 9-14.

[11] Karvonen, A, Taina, T., Gustafsson, J., Mannio, J., Mehtonen, J., Nystén, T., Ruoppa, M., Sainio, P., Siimes, K., Silvo, K., Tuominen, S., Verta, M., Vuori, K.M., Äystö, L. Vesiympäristölle vaarallisista ja haitallisista aineista annettujen säädösten soveltaminen - Kuvaus hyvistä menettelytavoista. Ympäristöministeriön raportteja 15/2012. Ympäristöministeriö. *Finnish Ministry of the Environment & SYKE*, 15:70, 2012. Vol. 15. p. 70.

[12] Ymparisto. Pohjavesitietojärjestelmä - ohjeita tiedontuottajille, 2012. URL http://www.ymparisto.fi/fi-FI/Kartat_ja_tilastot/Tietojarjestelmat/Pohjavesitietojarjestelma__ohjeita_tiedo(8279). [Cited 30 June 2017].

[13] European Environment Agency. Groundwater monitoring in Europe - Finland, 2016. URL https://www.eea.europa.eu/publications/92-9167-032-4/page006.html. [Cited 8 June 2017].

[14] Salonen, V. Mapping of groundwater reserves in Finland: The present status and aspects for future work. *Master's Thesis. University of Helsinki, Department of Geology*, 2002. Helsinki. pp. 56-57.

[15] Ymparisto. Groundwater in Finland, 2016. URL http://www.ymparisto.fi/en-US/Waters/Protection_of_waters/Groundwater_protection/Groundwater_in_Finland. [Cited 24 June 2017].

[16] SYKE. Groundwater area - SYKE, basemap database © national land survey of Finland, 2016. URL http://www.syke.fi/en-US. [Cited 22 February 2017].

[17] Sutter II, G.W., Tsao, C.L. Toxicological benchmarks for screening potential contaminants of concern for effects on aquatic biota: 1996 revision. *Oak Ridge National Laboratory (ORNL), Oak Ridge, Tennessee, Report ES/ER/TM-96/R2*, 9(1):151, 1996. Vol. 9:1. p. 151.

[18] PreventionWeb. Deterministic and probabilistic risk, 2015. URL http://www.preventionweb.net/risk/deterministic-probabilistic-risk. [Cited 20 June 2017].

[19] Lindhe, A. Risk assessment and decision support for managing drinking water systems. *PhD Thesis. Chalmers University of Technology; Department of Civil and Environmental Engineering, Division of Geoengineering*, 2010. Gothenburg. pp. 41-58.

[20] US EPA. Human health risk assessment, 2016. URL https://www.epa.gov/risk/human-health-risk-assessment. [Cited 1 June 2017].

[21] Sorvari, J., Schultz, E., Rossi, E., Lehtinen, H., Joutti, A., Vaajasaari, K., Kauppila, T. Risk assessment of natural and anthropogenic arsenic in the Pirkanmaa region, Finland. *SYKE, Esko Rossi Oy, Pirkanmaa Regional Environmental Center, GTK*, 2007. pp. 29-41.

[22] US EPA. NATA: Glossary of Terms, 2016. URL https://www.epa.gov/national-air-toxics-assessment/nata-glossary-terms. [Cited 21 June 2017].

[23] Hyvönen, A. Mikkeli - Pursialan pohjavesialueen tutkimukset Rakenne- ja virtausmallinnus. *GTK*, 2013. p. 44.

[24] Babiker, I.S., Mohamed, M.A.A., Hiyama, T., Kato, K. A GIS-based DRASTIC model for assessing aquifer vulnerability in Kakamigahara Heights, Gifu Prefecture, central Japan. *Science of The Total Environment*, 2005. Vol. 345. pp. 127-140.

[25] Vaezihir, A., Tabarmayeh, M. Total vulnerability estimation for the Tabriz aquifer (Iran) by combining a new model with DRASTIC. *Environmental Earth Sciences*, 2015. Vol. 74:4. pp. 2949-2965.

[26] Huan, H., Wang, J., Teng, Y. Assessment and validation of groundwater vulnerability to nitrate based on a modified DRASTIC model: A case study in Jilin City of northeast China. *Science of The Total Environment*, 2012. Vol. 440:1-2. pp. 14-23.

[27] Iqbal, J., Gorai, A.K., Tirkey, P., Pathak, G. Approaches to groundwater vulnerability to pollution: a literature review. *Asian J Water Environ Pollut*, 9(1): 127–140, 2012. Vol. 9:1. pp. 127-140.

[28] Kumar, S., Mathew, S., Radhakrishnan, N., Thirumalaivasan, D. Groundwater vulnerability assessment using SINTACS model. *Geomatics, Natural Hazards and Risk*, 2013. Vol. 4:4. pp. 339-354.

[29] Civita, M. Le carte della vulnerabilità degli acquiferi all'inquinamento. Teoria and pratica. *Pitagora Editrice, Bologna*, 1994. p. 325.

[30] Aller, L., Bennet, T., Lehr, J. H., Petty, R., Hacket, G. DRASTIC: a standardized system for evaluating groundwater pollution potential using hydrogeological settings. *US EPA*, 1987. Vol. 600/2-85/0108. p. 163.

[31] Rahman, A. GIS based DRASTIC model for assessing groundwater vulnerability in shallow aquifer in Aligarh, India. *Applied Geography*, 2008. Vol. 28:4. pp. 32-53.

[32] Luoma, S., Okkonen, J., Korkka-Niem, K. Comparison of the avi, modified sintacs and galdit vulnerability methods under future climate-change scenarios for a shallow low-lying coastal aquifer in southern finland. *Hydrogeology Journal*, 2017. Vol. 25:1. pp. 203-222.

[33] Gupta, N. Groundwater Vulnerability Assessment using DRASTIC Method in Jabalpur District of Madhya Pradesh. *International Journal of Recent Technology and Engineering*, 2014. Vol. 3:3. pp. 36-43.

[34] Jafari, S.M., Nikoo, M.R. Groundwater risk assessment based on optimization framework using DRASTIC method. *Arabian Journal of Geosciences*, 2016. Vol. 20:9. pp. 1-14.

[35] Lodwick, W.A., Monson, W., Svoboda, L. Attribute error and sensitivity analysis of map operations in geographical information systems: suitability analysis. *International Journal of Geographical Information Systems*, 1990. Vol. 4:4. pp. 413-428.

[36] Napolitano P., Fabbri A.G. Single-parameter sensitivity analysis for aquifer vulnerability assessment using DRASTIC and SINTACS. *Proceedings of the Vienna conference on HydroGIS 96: application of geographic information systems in hydrology and water resources management IAHS*, 1996. 253. pp. 559–566.

[37] Artimo, A., Salonen, V.P., Pietilä, S., Saraperä, S. Three-dimensional geologic modeling and groundwater flo wmodeling of the Töllinperä aquifer in the Hitura nickel mine area, Finland – providing the framework for restoration and protection of the aquifer. *Bulletin of the Geological Society of Finland*, 2004. Vol. 76. pp. 5-17.

[38] USGS. MODFLOW: USGS three-dimensional finite-difference ground-water model, 2017. URL https://water.usgs.gov/ogw/modflow/MODFLOW.html. [Cited 24 June 2017].

[39] Purjenaie, A., Moradi, M., Noruzi, A., Majidi, A. Prediction of aquifer drawdown using MODFLOW mathematical model (case study: Sarze Rezvan Plain, Iran). *Geosciences*, 2012. Vol. 5:2. pp. 112-116.

[40] Artimo, A. Application of fl ow and transport models to the polluted Honkala aquifer, Säkylä, Finland. *Boreal Environment Research*, 7:161–172, 2002. Vol. 7:7. pp. 161-172.

[41] Saghravani, S.R., Mustapha, S. Prediction of contamination migration in an unconfined aquifer with Visual MODFLOW: A case study. *World Applied Sciences Journal*, 2011. Vol. 14:7. pp. 1102-1106.

[42] Newell, C.J., McLeod, R.K., Gonzales, J.R.,. BIOSCREEN - Natural attenuation decision support system. User's manual version 1.4. *US EPA*, 1996. pp. 1-16.

[43] US EPA. Case study for the use of a decision support tool: Naval air station Lemoore, California. *US EPA*, 2005. pp. 1-14.

[44] Akins, C.R., Striegel, J.A., Sanders, D. A., Veenstra, J.N. Modeling natural attenuation of petroleum hydrocarbon contamination using alternate electron acceptors: Case study comparing bioplume iii with BIOSCREEN. *Remediation Journal*, 2000. Vol. 10:4. pp. 27-47.

[45] Kjeldsen, P. Estimation methods for sorption of organic pollutants in soil and groundwater. *Lecture note for 12330 Soil and Groundwater Pollution – Processes and Remediation. Department of Environmental Engineering. Technical University of Denmark (DTU)*, 2012. pp. 2-13.

[46] Piwoni, M.D., Keeley, J.W. Basic concepts of contaminant sorption at hazardous waste sites. *US EPA*, 1990. p. 7.

[47] US EPA - Office of Radiation and Indoor Air, Office of Solid Waste and Emergency Response; U.S. Department of Energy - Office of Environmental Restoration. Volume I: The Kd model, methods of measurement, and application of chemical reaction codes. *US EPA*, 1999. p. 212.

[48] Schwarzenbach, R.P., Gschwend, P.M., Imboden, D.M. Environmental organic chemistry. *John Wiley & Sons: Hoboken*, 2003.

[49] FAO. Assessing soil contamination - A reference manual, 2000. URL http://www.fao.org/docrep/003/X2570E/X2570E06.htm. [Cited 17 February 2017].

[50] Yamamoto, H. Octanol-water partition coefficient, 2004. URL https://www.pirika.com/ENG/TCPE/logP-Theory.html. [Cited 8 March 2017].

[51] Abdul, A.S., Gibson, T.L., Rai, D.N. Statistical correlations for predicting the partition coefficient for nonpolar organic contaminants between aquifer organic carbon and water. *Hazardous Waste & Hazardous Materials*, 1987. Vol. 4. pp. 211-222.

[52] Jafvert, C.T. Sorption of organic acid compounds to sediments: Initial model development. *Environmental Toxicology and Chemistry*, 1990. Vol. 9:10. pp. 1259-1268.

[53] Jafvert, C.T., Weber, E.J. Sorption of ionizable organic coumpounds to sediments and soils. *US EPA*, 1991. US EPA/600/S3-91/017.

[54] Kulkarni, M.N., Nanda, H.S., Ramakrishnegowda, C., Sivapullaiah, P.V. Soil bentonite liner to control migration of sodium and potassium ions. *Research in Chemistry and Environment*, 2016. p. 8.

[55] Mikkeli, 2017. URL http://www.mikkeli.fi/. [Cited 26 January 2017].

[56] WaterHope. Mikkelin entinen kyllästämö: PAH-yhdisteiden kulkeutumisen ja käyttäytymisen laskenta. Mallinnuksen loppuraportti, 20.11.2013 (unpublished consulting report in Finnish). *WaterHope*, 2013.

[57] NC Environmental Quality. Groundwater standards, 2017. URL https://deq.nc.gov/about/divisions/water-resources/planning/classification-standards/groundwater-standards{#}How{_}are{_}GW{_}stds{_}established. [Cited 21 June 2017].

[58] New Jersey Department of Environmental Protection. Groundwater quality standards - Class IIA, 2016. URL http://www.nj.gov/dep/standards/groundwater.pdf. [Cited 21 June 2017].

[59] ATSDR. Public health statement: Chlorophenols (CPHs), 1999. URL https://www.atsdr.cdc.gov/PHS/PHS.asp?id=939{&}tid=195. [Cited 28 January 2017].

[60] WHO. Chlorophenols in driking-water. *Guidelines for Drinking-Water Quality - Second Edition - Volume 2 - Health Criteria and Other Supporting Information*, 1998. Vol. 2. pp. 1-7.

[61] ChemSpider, Search and Share Chemistry. Search ChemSpider - 2-Chlorophenol, 2,4-Dichlorophenol, 2,3,4-Trichlorophenol, 2,3,4,6-Tetrachlorophenol, Pentachlorophenol, Acenaphthene, Anthracene, Benzo(a)pyrene, Chrysene, Fluoranthene, Fluorene, Naphthalene, Phenanthrene, Pyrene, 2017. URL http://www.chemspider.com. [Cited 3 June 2017].

[62] The PubChem Project. PubChem database - 2-Chlorophenol, 2,4-Dichlorophenol, 2,3,4-Trichlorophenol, 2,3,4,6-Tetrachlorophenol, Pentachlorophenol, Acenaphthene, Anthracene, Benzo(a)pyrene, Chrysene, Fluoranthene, Fluorene, Naphthalene, Phenanthrene, Pyrene, 2004. URL https://pubchem.ncbi.nlm.nih.gov. [Cited 28 March 2017].

[63] Hooiveld, M., Heederik, D.J., Kogevinas, M., Boffetta, P., Needham, L.L., Patterson, D.G. Jr, Bueno-de-Mesquita, H.B. Second follow-up of a Dutch cohort occupationally exposed to phenoxyherbicides, chlorophenols, and contaminants). *American Journal of Epidemiology*, 1998. Vol. 147:9. pp. 891-899.

[64] Lampi, P., VohlonenJuoko, I., Tuomisto, J., Heinonen, O.P. Increase of specific symptoms after long-term use of chlorophenol polluted drinking water in a community). *European Journal of Epidemiology*, 2000. Vol. 16:3. pp. 245-251.

[65] Wagner, S.L., Durand, L.R., Deinzer, M.L., Inman, R.D., Kiigemagi, U. Residues of pentachlorophenol and other chlorinated contaminants in human tissues: analysis by electron capture gas chromatography and electron capture negative ion mass spectrometry). *J Hazard Mater*, 1991. Vol. 21:4. pp. 596-606.

[66] ATSDR. Public health statement: Polycyclic Aromatic Hydrocarbons (PAHs), 1995. URL https://www.atsdr.cdc.gov/PHS/PHS.asp?id=120{&}tid=25. [Cited 27 March 2017].

[67] H.I. Abdel-Shafy and M.S.M. Mansour. A review on polycyclic aromatic hydrocarbons: Source, environmental impact, effect on human health and remediation. *Egyptian Journal of Petroleum*, 2016. Vol. 25:1. pp. 1107-123.

[68] WHO. Polynuclear aromatic hydrocarbons in drinking-water. *Guidelines for Drinking-Water Quality - Second Edition - Volume 2 - Health Criteria and Other Supporting Information*, 1998. Vol. 2. pp. 18-19.

[69] Southworth, G.R. The role of volatilization in removing polycyclic aromatic hydrocarbons from aquatic environments. *Bulletin of environmental contamination and toxicology*, 1979. Vol. 21. pp. 507-514.

[70] US EPA. Buha, A., 2011. URL http://www.toxipedia.org/display/toxipedia/Polycyclic+Aromatic+Hydrocarbons. [Cited 22 June 2017].

[71] Rengarajan, T., Rajendran, P., Nandakumar, N., Lokeshkumar, B., Nishigaki, I., Rajendran, P. Exposure to polycyclic aromatic hydrocarbons with special focus on cancer). *J Hazard Mater,*, 2015. Vol. 5:3. pp. 182-189.

[72] Khairy, M.A., Kolb, M., Mostafa, A.R., El-Fiky, A., Bahadir, M. Risk assessment of polycyclic aromatic hydrocarbons in a Mediterranean semi-enclosed basin affected by human activities (Abu Qir Bay, Egypt). *J Hazard Mater,*, 2009. Vol. 170:1. pp. 389-397.

[73] US EPA. How to evaluate alternative cleanup technologies for underground storage tank sites: A guide for corrective action plan reviewers. *US EPA*, 2004. US EPA 510-B-94-003; US EPA 510-B-95-007; US EPA 510-R-04-002; US EPA 510-B-16-005.

[74] Boopathy, R. Factors limiting bioremediation technologies. *Bioresource Technology*, 2000. Vol. 74:1. pp. 63-67.

[75] Pacific Northwest National Laboratory. In situ bioremediation, 2012. URL http://bioprocess.pnnl.gov/resour/rt3d.in.situ.bioremediation.htm. [Cited 13 March 2017].

[76] Bioremediation of DNAPLs Team. In situ bioremediation of chlorinated ethene: DNAPL source zones. *The Interstate Technology & Regulatory Council*, 2008. p. 133.

[77] US EPA. A citizens's guide to In SItu Chemical Oxidation, 2012. URL https://clu-in.org/download/Citizens/a_citizens_guide_to_in_situ_chemical_oxidation.pdf. [Cited 30 June 2017].

[78] Bjerg, P.L., Hønning, J., Tsitonaki, A. In situ chemical oxidation. *Lecture note for 12330 Contaminated sites. Department of Environmental Engineering. Technical University of Denmark (DTU)*, 2009. pp. 19-22.

[79] SIREM. In Situ Chemical Oxidation (ISCO), 2017. URL http://www.siremlab.com/in-situ-chemical-oxidation-isco/. [Cited 30 June 2017].

[80] Bedient, P.B., Rifai, H., Newell, C.J. Groundwater contamination: transport and remediation. *Prentice Hall*, 1999. pp. 339-340.

[81] Wang, H., Liu, S., Du, S. The investigation and assessment on groundwater organic pollution, 2013. URL https://www.intechopen.com/books/organic-pollutants-monitoring-risk-and-treatment/the-investigation-and-assessment-on-groundwater-organic-pollution. [Cited 22 May 2017].

[82] Townsend, C., Sherril, R. Soil and groundwater remediation, 2012. URL http://www.sageenvironmental.com/assets/pdf/Service_Sheets/Groundwater/Soil_Groundwater_Remediation_Service_Sheet_VIEW.pdf. [Cited 22 June 2017].

[83] US EPA. A citizen's guide to pump and treat. Office of solid waste and emergency response. *US EPA*, 2001. US EPA 542-F-01-025.

[84] Committee on Ground Water Cleanup Alternatives, Water Science and Technology Board, Board on Radioactive Waste Management, Commission on Geosciences, Environment, and Resources. Alternatives for groundwater cleanup. *National Academy Press - Washington, D.C.*, 1994. pp. 80-124.

[85] Mitikka, S., Britschgi, R., Granlund, K., Grönroos, J., Kauppila, P., Mäkinen, R., Niemi, J., Pyykkönen, S., Raateland, A., Silvo, K. Report on the implementation of the nitrates directive in finland 2004. *SYKE*, 2005. pp. 70-71.

[86] SYKE. Avoimet ympäristötietojärjestelmät, 2016. URL http://www.syke.fi/fi-FI/Avoin_tieto/Ymparistotietojarjestelmat. [Cited 3 March 2017].

[87] Finnish Consulting Group (FCG), 2017. URL http://www.fcg.fi. [Cited 5 June 2017].

[88] Al-Zabet, T. Evaluation of aquifer vulnerability to contamination potential using the DRASTIC method. *Environmental Geology*, 2002. Vol. 43:1-2. pp. 203-208.

[89] Lee, S. Evaluation of waste disposal site using the DRASTIC system in Southern Korea. *Environmental Geology*, 2003. Vol. 44:6. pp. 654-664.

[90] Ali, S.S., Hamamin, D.F. Groundwater vulneraility map of Basara basin, Sulaimani Governorate, Iraqui Kurdistan Region. *Iraqi Journal of Science*, 2012. Vol. 54:3. pp. 579-594.

[91] Rosen, L. Study of the DRASTIC methodology with the emphasis on Swedish conditions. *In Program and abstracts of the 37th conference of the International Association for Great Lakes Research and Estuarine Research Federation. Buffalo, NY: IAGLR*, 1994. p. 166.

[92] Locatelli, L., Rosenberg, L., Bjerg, P.L., Binning, P.J. Grundrisk coupling of vertical and horizontal transport models. *Miljøstyrelsen*, 2016. pp. 13-32.

[93] Rosenberg, L., Søndergaard, G.L., Binning, P.J., Aabling, J., Bjerg, P.L. Grundrisk - beregningsmodel til risikovurdering af grundvandstruende forureninger. *Miljøstyrelsen*, 2016. Vol. 1865. pp. 25, 102, 103.

[94] Bjerg, P.L. Dispersion in aquifers. *Lecture note for 12330 Soil and Groundwater Pollution – Processes and Remediation. Department of Environmental Engineering. Technical University of Denmark (DTU)*, 2013. p. 1.

[95] Mackay, D., Shiu, W.Y., Ma, K.C. Illustrated handbook of physical-chemical properties and environmental fate for organic chemicals: Polynuclear aromatic hydrocarbons, polychlorinated dioxins and dibenzofurans. *CRC Press, Taylor & Francis Group*, 1992. pp. 640-690.

[96] Howard, P.H., Boethling, R.S., Jarvis, W.F., Meylan, W.M., Michalenko, E.M. Handbook of environmental degradation rates. *Lewis Publishers, Inc., Chelsea, MI*, 1991. pp. 12, 218, 226, 236, 260, 460, 506, 546, 552.

[97] Boguski, T. Public health assessment guidance manual, 2005. URL https://www.engg.ksu.edu/chsr/files/chsr/tosc/healthrisk.pdf. [Cited 1 June 2017].

[98] US EPA. Exposure factors handbook, 1997. URL https://www.epa.gov/aboutepa/about-national-center-environmental-assessment-ncea. [Cited 20 June 2017].

[99] US EPA. IRIS database - 2-Chlorophenol, 2,4-Dichlorophenol, 2,3,4-Trichlorophenol, 2,3,4,6-Tetrachlorophenol, Pentachlorophenol, Acenaphthene, Anthracene, Benzo(a)pyrene, Chrysene, Fluoranthene, Fluorene, Naphthalene, Phenanthrene, Pyrene, 2017. URL https://cfpub.epa.gov/ncea/iris2/atoz.cfm. [Cited 2 June 2017].

[100] US EPA. Updated dermal exposure assessment guidance, 2016. URL https://www.epa.gov/risk/updated-dermal-exposure-assessment-guidance. [Cited 26 June 2017].

[101] US EPA. Dermal exposure assessment: Principles and applications. *US EPA*, 1992. US EPA/600/8-91/011B.

[102] US EPA. Risk assessment guidance for superfund, supplemental guidance for dermal risk assessment - Part E, 2016. URL https://19january2017snapshot.epa.gov/risk/risk-assessment-guidance-superfund-rags-part-e_.html. [Cited 11 June 2017].

[103] GSI Environmental Inc. GSI chemical properties database - 2-Chlorophenol, 2,4-Dichlorophenol, 2,3,4-Trichlorophenol, 2,3,4,6-Tetrachlorophenol, Pentachlorophenol, Acenaphthene, Anthracene, Benzo(a)pyrene, Chrysene, Fluoranthene, Fluorene, Naphthalene, Phenanthrene, Pyrene, 2017. URL http://www.gsi-net.com/en/publications/gsi-chemical-database.html. [Cited 4 June 2017].

[104] US EPA. Risk assessment guidance for superfund volume I: Human health evaluation manual (Part A), 1989. URL http://rais.ornl.gov/documents/HHEMA.pdf. [Cited 15 July 2017].

[105] Liggett, J.E., Talwar, S. Groundwater vulnerability assessments and integrated water resource management, Streamline Watershed Management. *Streamline Watershed Management Bulletin*, 2009. Vol. 13:1. pp. 18-29.

[106] Villarini, G. Inference of spatial scaling properties of rainfall: Impact of radar rainfall estimation uncertainties. *EEE Geosci. Remote Sens. Lett*, 2009. Vol. 6:4. pp. 812-815.

[107] USGS. Unsaturated flow processes, 2013. URL https://wwwrcamnl.wr.usgs.gov/uzf/investigations/investigations.html. [Cited 26 June 2017].

[108] Wellman, D.M., Freshley, M.D., Johnson, T.C., Miracle, A.L. Contaminants in vadose zone environments. *Soil Science Society of America*, 2012. pp. 1-3.

[109] Dresel, P.E., Wellman, D.M., Cantrell, K.J., Truex M.J. Review: Technical and policy challenges in deep vadose zone remediation of metals and radionuclides. *Environ. Sci. Technol*, 2011. Vol. 45:10. pp. 4207-4216.

[110] Harter, T., Walker, L.G. Assessing vulnerability of groundwater, 2017. URL http://groundwater.ucdavis.edu/files/136263.pdf. [Cited 18 June 2017].

[111] US EPA. Exposure factors handbook: 2011 edition. *US EPA*, 2011. pp. 487-534.

Appendices

Appendix 1 - Appendix 1 - Concentrations detected in the sawmill area. 2 pages

Appendix 2 - GrundRisk model. 4 pages

Appendix 3 - GrundRisk results for PAHs. 4 pages

Appendix 4 - Calculation of human health risks. 10 pages

Appendix 1 - Concentrations detected in the sawmill area

Table 1: Concentrations of Chlorophenols (CPs) detected in wells installed by the Finnish Consulting Group in the Pursiala aquifer. The value is highlighted in blue if it is above the groundwater guideline - first part [87]

Well M14 - 27 samples

Chemical	Unit	Groundwater guideline	Max	Min	Mean	STDV	95% UCL
2-CP	μg/l	40	6.1E+01	0	8.1E+00	1.8E+01	4.4E+01
2,4-DCP	μg/l	20	2.0E+02	2.3E-01	3.4E+01	5.8E+01	1.5E+02
2,4,6-TCP	μg/l	1	3.0E+03	5.0E-02	2.6E+02	6.2E+02	1.5E+02
2,3,4,6-TeCP	μg/l	200	1.0E+05	6.0E-01	8.5E+03	2.0E+04	4.9E+04
PCP	μg/l	0.3	2.4E+03	3.0E-01	2.9E+02	4.9E+02	1.3E+03

Well HP9 - 34 samples

Chemical	Unit	Groundwater guideline	Max	Min	Mean	STDV	95% UCL
2-CP	μg/l	40	3.7E+00	0	1.1E+00	9.0E-01	3.1E+00
2,4-DCP	μg/l	20	1.6E+02	3.1E+00	3.9E+01	3.2E+01	1.0E+02
2,4,6-TCP	μg/l	1	2.2E+03	5.1E+01	5.5E+02	4.8E+02	1.5E+03
2,3,4,6-TeCP	μg/l	200	5.9E+04	1.1E+03	1.3E+04	1.3E+04	4.0E+04
PCP	μg/l	0.3	1.6E+03	1.5E+02	5.7E+02	3.8E+02	1.3E+03

Well 89 - 21 samples

Chemical	Unit	Groundwater guideline	Max	Min	Mean	STDV	95% UCL
2-CP	μg/l	40	6.0E-01	1.0E-01	3.0E-01	1.0E-01	6.0E-01
2,4-DCP	μg/l	20	5.3E+00	3.3E+00	4.2E+00	7.0E-01	5.6E+00
2,4,6-TCP	μg/l	1	2.8E+01	1.0E+01	1.8E+01	5.5E+00	2.9E+01
2,3,4,6-TeCP	μg/l	200	6.2E+02	9.5E+00	1.3E+02	1.9E+02	5.1E+02
PCP	μg/l	0.3	3.1E+01	5.0E-01	8.1E+01	1.0E+01	2.9E+01

Well 91 - 20 samples

Chemical	Unit	Groundwater guideline	Max	Min	Mean	STDV	95% UCL
2-CP	μg/l	40	1.8E+01	9.3E+00	1.1E+01	3.2E+00	1.7E+01
2,4-DCP	μg/l	20	2.9E+02	1.4E+02	2.0E+02	4.7E+01	2.9E+02
2,4,6-TCP	μg/l	1	1.7E+02	9.5E+01	1.3E+02	2.9E+01	1.9E+02
2,3,4,6-TeCP	μg/l	200	1.5E+02	6.1E+01	1.1E+02	3.5E+01	1.8E+02
PCP	μg/l	0.3	6.3E+00	1.7E+00	3.9E+00	1.8E+00	7.5E+00

Table 2: Concentrations of Chlorophenols (CPs) detected in wells installed by the Finnish Consulting Group in the Pursiala aquifer. The value is highlighted in blue if it is above the groundwater guideline - second part [87]

Well 113 - 16 samples

Chemical	Unit	Groundwater quality	Max	Min	Mean	STDV	95% UCL
2-CP	μg/l	40	1.0E-01	0	1.0E-01	1.0E-01	1.0E-01
2,4-DCP	μg/l	20	3.7E+00	2.4E+00	3.1E+00	6.0E-01	4.4E+00
2,4,6-TCP	μg/l	1	3.6E+01	2.2E+01	2.9E+01	7.4E+00	4.4E+01
2,3,4,6-TeCP	μg/l	200	4.8E+02	3.0E+02	4.2E+02	1.0E+02	6.3E+02
PCP	μg/l	0.3	6.6E+01	4.4E+01	5.4E+01	1.1E+01	7.6E+01

Well 115 - 30 samples

Chemical	Unit	Groundwater guideline	Max	Min	Mean	STDV	95% UCL
2-CP	μg/l	40	8.3E+00	1.0E-01	1.9E+00	2.1E+00	6.1E+00
2,4-DCP	μg/l	20	1.5E+02	1.0E-01	4.7E+01	4.0E+01	1.3E+02
2,4,6-TCP	μg/l	1	3.1E+03	1.2E+00	8.0E+02	8.4E+02	2.5E+03
2,3,4,6-TeCP	μg/l	200	2.1E+04	7.6E+00	5.6E+03	6.2E+03	1.8E+04
PCP	μg/l	0.3	1.3E+03	1.1E+00	2.9E+02	3.3E+02	9.5E+02

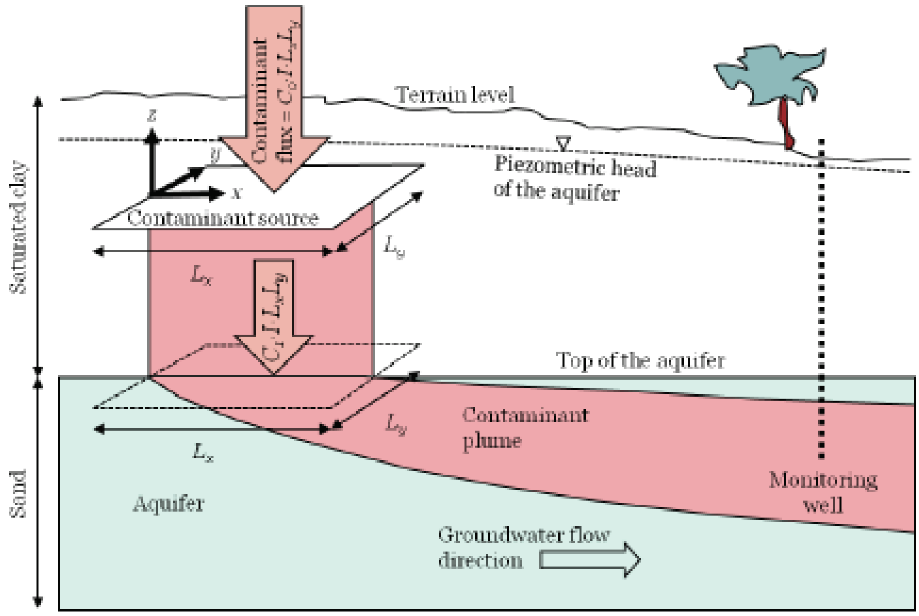
Well S2 - 4 samples

Chemical	Unit	Groundwater quality	Max	Min	Mean	STDV	95% UCL
2-CP	μg/l	40	0	0	-	-	-
2,4-DCP	μg/l	20	4.5E+01	1.5E+00	18.3	2.3E+01	6.5E+01
2,4,6-TCP	μg/l	1	1.2E+02	3.0E+01	7.0E+01	4.6E+01	1.6E+02
2,3,4,6-TCP	μg/l	200	5.5E+02	4.3E+02	5.0E+02	6.1E+01	6.2E+02
PCP	μg/l	0.3	5.7E+01	3.2E+01	4.8E+01	1.4E+01	7.5E+01

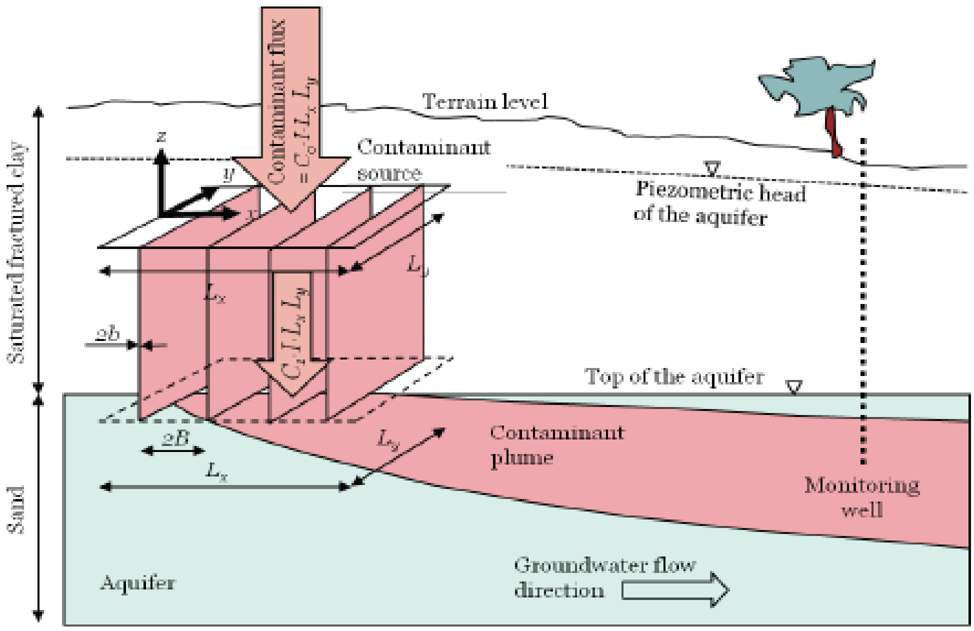
Well S3 - 4 samples

Chemical	Unit	Groundwater guideline	Max	Min	Mean	STDV	95% UCL
2-CP	μg/l	40	3.9E+02	1.1E+00	1.3E+02	2.2E+02	5.8E+02
2,4-DCP	μg/l	20	1.3E+02	1.6E+01	5.5E+01	6.7E+01	1.9E+02
2,4,6-TCCP	μg/l	1	2.8E+02	1.2E+02	1.9E+02	8.3E+01	3.5E+02
2,3,4,6-TeCP	μg/l	200	2.2E+03	5.1E+02	1.1E+03	9.5E+02	3.0E+03
PCP	μg/l	0.3	1.2E+02	2.9E+01	6.3E+01	5.0E+01	1.6E+02

Appendix 2 - GrundRisk model

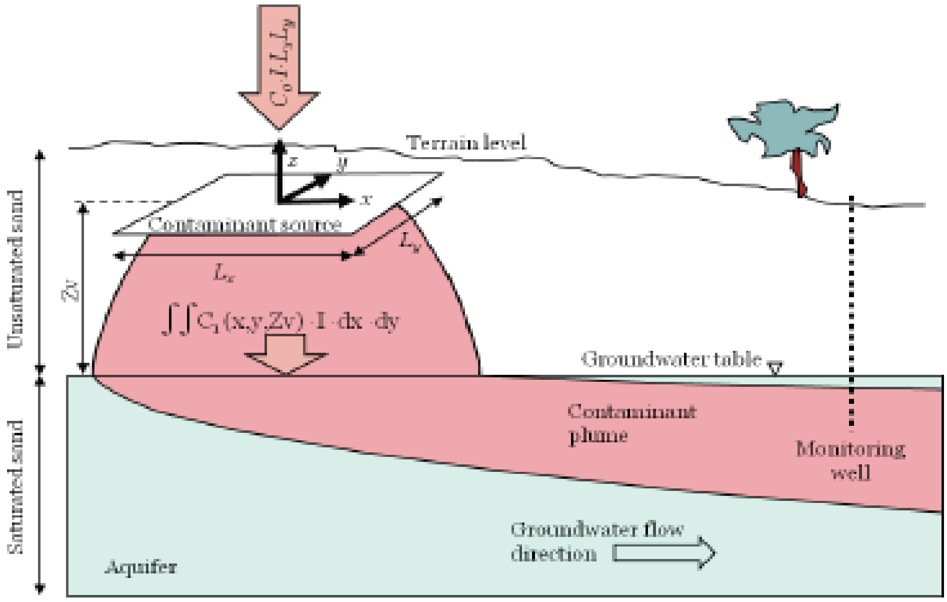


(a) Model number I

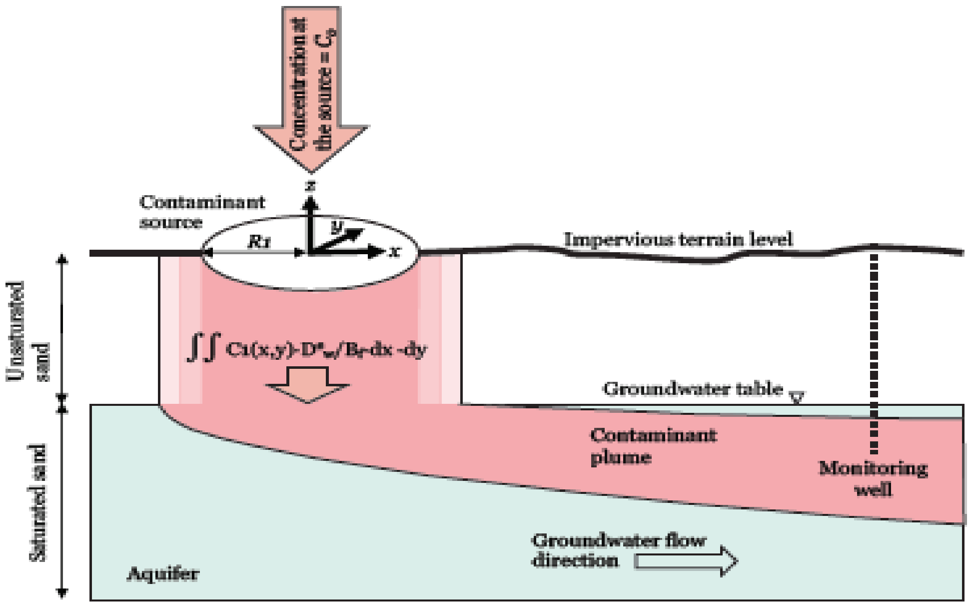


(b) Model number II

Figure 1: GrundRisk conceptual model number I and II [92]



(a) Model number III



(b) Model number IV

Figure 2: GrundRisk conceptual model number III and IV [92]

Table 3: Concentrations of Polycyclic Aromatic Hydrocarbons (PAHs) detected in well 31R, 35R, 42R, 50R of the POVET database installed in the area around the wood impregnation plant. The value is highlighted in blue if it is above the groundwater guideline [86]

31R, 25 m from the source area (SA) in the aquifer - 34 samples

Chemical	Unit	Groundwater	Max	Min	Mean	STDV	95% UCL
Acenaphthene	$\mu g/l$	400	4.7E-01	1.0E-01	1.9E-01	1.3E-01	4.5E-01
Anthracene	$\mu g/l$	2000	< 1.0E-01	< 1.0E-01	< 1.0E-01	-	-
Benzo(a)pyrene	$\mu g/l$	0.005	< 1.0E-01	< 1.0E-01	< 1.0E-01	-	-
Chrysene	$\mu g/l$	5	< 1.0E-01	< 1.0E-01	< 1.0E-01	-	-
Fluoranthene	$\mu g/l$	300	< 1.0E-01	< 1.0E-01	< 1.0E-01	-	-
Fluorene	$\mu g/l$	300	2.0E-01	1.0E-01	1.0E-01	1.0E-01	2.0E-01
Naphthalene	$\mu g/l$	300	1.3E+00	2.0E-01	4.0E-01	5.0E-01	1.4E+00
Phenanthrene	$\mu g/l$	100	3.0E-01	3.0E-01	3.0E-01	-	-
Pyrene	$\mu g/l$	200	< 1.0E-01	< 1.0E-01	< 1.0E-01	-	-

35R, 200 m from the source area (SA) in the aquifer - 6 samples

Chemical	Unit	Groundwater	Max	Min	Mean	STDV	95% UCL
Acenaphthene	$\mu g/l$	400	3.5E+02	1.0E+02	2.3E+02	9.7E+01	4.2E+02
Anthracene	$\mu g/l$	2000	2.6E+02	7.0E-01	1.5+00	8.0E-01	3.1E+00
Benzo(a)pyrene	$\mu g/l$	0.005	< 1.0E-01	< 1.0E-01	< 7.0E-01	-	-
Chrysene	$\mu g/l$	5	< 1.0E-01	< 1.0E-01	< 1.0E-01	-	-
Fluoranthene	$\mu g/l$	300	2.1E+00	3.0E-01	1.1E+00	7.0E-01	2.5E+00
Fluorene	$\mu g/l$	300	1.0E+02	3.8E+01	6.8E+01	2.6E+01	1.2E+02
Naphthalene	$\mu g/l$	300	9.7E+02	6.9E+01	4.2E+02	3.7E+02	1.1E+03
Phenanthrene	$\mu g/l$	100	4.3E+01	1.1E+01	2.4E+01	1.3E+01	5.0E+01
Pyrene	$\mu g/l$	200	8.0E-01	1.0E-01	4.0E-01	3.0E-01	9.0E-01

Well 42R, 400 m from the source area (SA) in the aquifer - 6 samples

Chemical	Unit	Groundwater	Max	Min	Mean	STDV	95% UCL
Acenaphthene	$\mu g/l$	400	3.0E+02	2.1E+02	2.6E+02	3.4E+01	3.3E+02
Anthracene	$\mu g/l$	2000	1.2E+00	8.0E-01	9.0E-01	1.0E-01	1.1E+00
Benzo(a)pyrene	$\mu g/l$	0.005	< 1.0E-01	< 1.0E-01	< 1.0E-01	-	-
Chrysene	$\mu g/l$	5	< 1.0E-01	< 1.0E-01	< 1.0E-01	-	-
Fluoranthene	$\mu g/l$	300	< 1.0E-01	< 1.0E-01	< 1.0E-01	-	-
Fluorene	$\mu g/l$	300	1.0E+02	7.3E+01	8.9E+01	9.8E+00	1.1E+02
Naphthalene	$\mu g/l$	300	2.2E+02	1.1E+02	1.7E+02	4.7E+01	2.7E+02
Phenanthrene	$\mu g/l$	100	4.2E+01	3.6E+01	4.0E+01	2.3E+00	4.4E+01
Pyrene	$\mu g/l$	200	< 1.0E-01	< 1.0E-01	< 1.0E-01	-	-

Well 50R, 500 m from the source area (SA) in the aquifer (point of compliance, POC) - 3 samples

Chemical	Unit	Groundwater	Max	Min	Mean	STDV	95% UCL
Acenaphthene	$\mu g/l$	400	6.0E-01	1.0E-01	4.0E-01	3.0E-01	1.1E+00
Anthracene	$\mu g/l$	2000	< 1.0E-01	< 1.0E-01	< 1.0E-01	-	-
Benzo(a)pyrene	$\mu g/l$	0.005	< 1.0E-01	< 1.0E-01	< 1.0E-01	-	-
Chrysene	$\mu g/l$	5	< 1.0E-01	< 1.0E-01	< 1.0E-01	-	-
Fluoranthene	$\mu g/l$	300	1.0E-01	< 1.0E-01	< 1.0E-01	-	-
Fluorene	$\mu g/l$	300	2.0E-01	2.0E-01	2.0E-01	-	-
Naphthalene	$\mu g/l$	300	5.0E-01	5.0E-01	5.0E-01	-	-
Phenanthrene	$\mu g/l$	100	1.0E-01	1.0E-01	1.0E-01	-	-
Pyrene	$\mu g/l$	200	< 1.0E-01	< 1.0E-01	< 1.0E-01	-	-

Table 4: GrundRisk variables for the case of the Polycyclic Aromatic Hydrocarbons (PAHs)

Variable	**Value**
A [$\mathbf{m}^2$]	900 - 2500
α_l **[m]**	3 - 10
α_t **[m]**	0.3 - 2
α_v **[m]**	0.5 - 2
B [m]	7 - 12
$\mathbf{D}_x$ [$\mathbf{m}^2/\mathbf{d}$]	1.5 - 10
$\mathbf{D}_y$ [$\mathbf{m}^2/\mathbf{d}$]	0.15 - 2
$\mathbf{D}_z$ [$\mathbf{m}^2/\mathbf{d}$]	0.25 - 2
$\mathbf{f}_{oc}$ **[-]**	2E-03 - 6E-03
I [m/d]	8.2E-04 - 9.9E-04
$\mathbf{K}_d$ [$\mathbf{cm}^3/\mathbf{g}$]	Depends on the chemical
$\mathbf{L}_x$ **[m]**	30 - 50
$\mathbf{L}_y$ **[m]**	30 - 50
M [g/d]	Depends on the chemical
n [-]	0.25 - 0.3
R [-]	Depends on the chemical
ρ_b [$\mathbf{g}/\mathbf{cm}^3$]	1.6 - 1.9
u [m/d]	0.5 - 1.0

Table 5: Specific variables of Polycyclic Aromatic Hydrocarbons (PAHs) [96] [95]

Chemical	C_0 [μg/l]	**M [g/d]**	**log** $\mathbf{K}_{ow}$ **[-]**	$\mathbf{K}_d$ [$\mathbf{cm}^3/\mathbf{g}$]	**R [-]**
Acenaphthene	1460	1.1 - 3.6	3.9	3.4 - 10.3	23.1 - 67.2
Anthracene	180	0.1 - 0.4	4.5	12.2 - 45.7	98.4 - 293.3
Benzo(a)pyrene	54	0.04 - 0.13	5.9	404.9 - 1214.9	2592.8 - 7776.5
Chrysene	171	0.13 - 0.42	5.91	404.9 - 1214.9	2592.8 -7776.5
Fluoranthene	823	0.6 - 2.0	5.2	77.6 - 232.7	497.6 - 1490.8
Fluorene	1050	0.8 - 2.5	4.2	6.4 - 19.3	42.1 - 124.5
Naphthalene	813	0.6 - 2.0	3.4	0.9 - 2.8	6.9- 18.7
Phenanthrene	1640	1.2 - 4.0	4.6	16.4 - 49.1	105.7 - 315.1
Pyrene	584	0.4 - 1.4	5.2	70.5 - 211.5	452.2 - 1354.7

Chemical	$\mathbf{t}_{1/2}$ **in groundwater**	$\mathbf{t}_{1/2}$ **aer. biod.**	$\mathbf{t}_{1/2}$ **anaer. biod.**	λ **[1/day]**
Acenaphthene	24.6 - 204 days	12.3 - 102 d	49.2 - 408 d	3.4E-03 - 1.7E-03
Anthracene	100 days - 2.52 y	50 d - 1.26 y	200 d - 5.04 y	3.8E-04 - 6.9E-03
Benzo(a)pyrene	114 days - 2.90 y	57 d - 1.45 y	228 d - 5.8 y	3.5E-04 - 1.2E-02
Chrysene	2.0 - 5.5 y	1.0 - 2.72 y	4.06 - 11.0 y	1.7E-04 - 1.2E-02
Fluoranthene	280 d - 2.4 y	140 - 440 d	1.5 - 4.8 y	3.9E-04 - 4.95E-03
Fluorene	64 - 120 d	32 - 60 d	128 - 240	2.9E-03 - 2.2E-02
Naphthalene	1 - 258 d	0.5 - 20 d	25 - 258 d	2.7E-03 - 6.9E-01
Phenanthrene	32 d - 1.1 y	16 - 200 d	64 h - 2.2 y	8.7E-04 - 2.2E-02
Pyrene	1.1 - 10.4 y	210 d - 5.2 y	2.3 - 28 y	3.0E-03 - 6.8E-05

Appendix 3 - GrundRisk results for PAHs

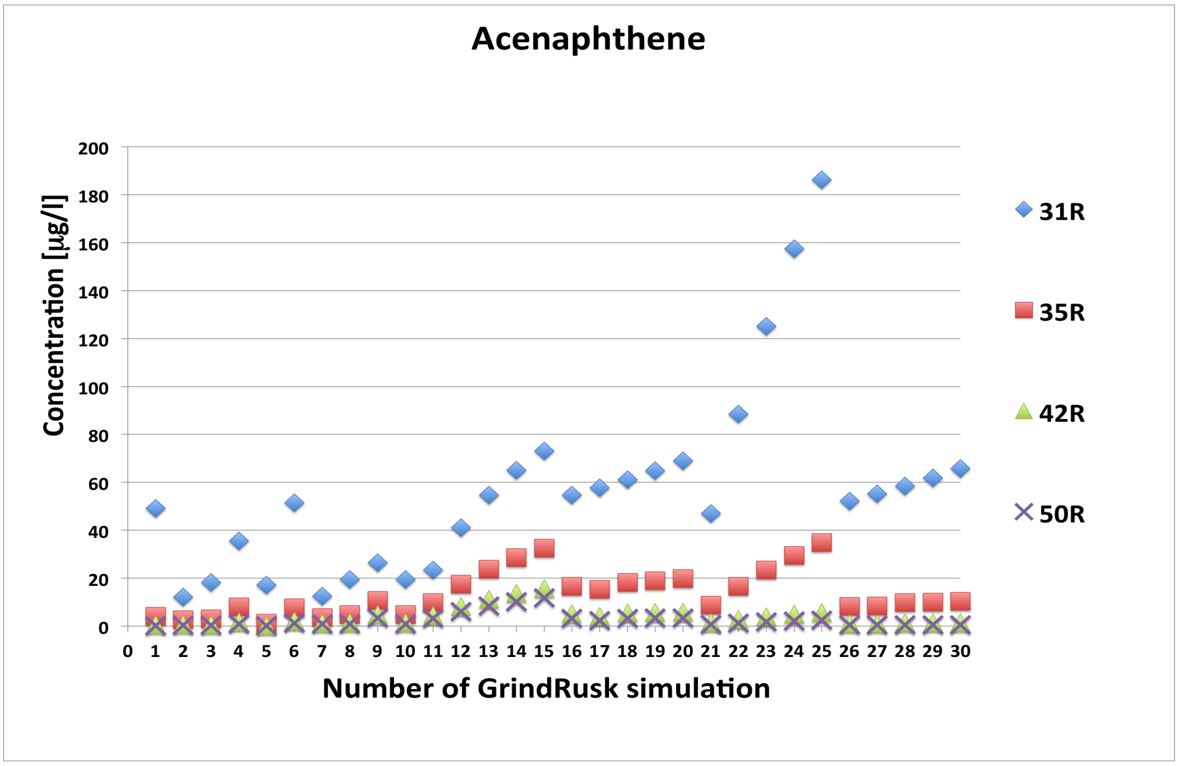
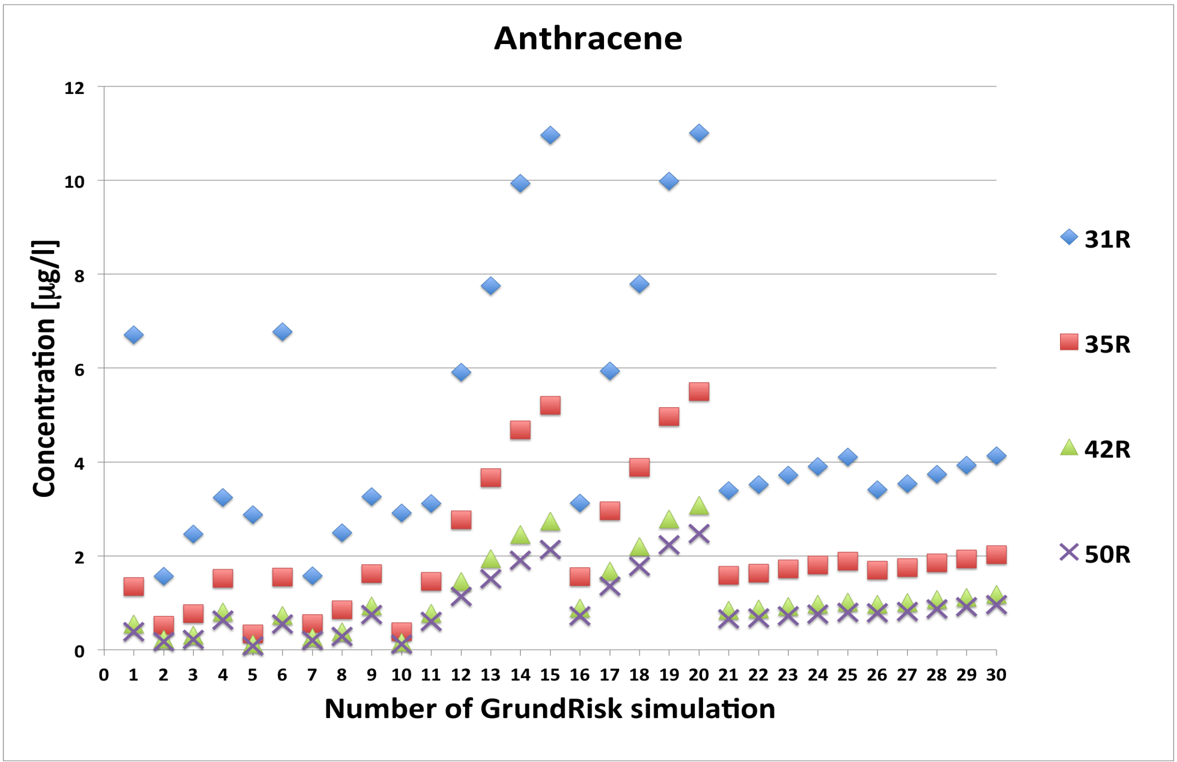


Figure 3: Acenaphthene concentrations obtained in each of the 30 GrundRisk simulations for well 31R, 35R, 42R and 50R. All the results are below the groundwater guidelines, i.e. 400 μg/l. The number of the simulation is on the x-axis, and each point of the graph is the concentration obtained for the well in the simulation



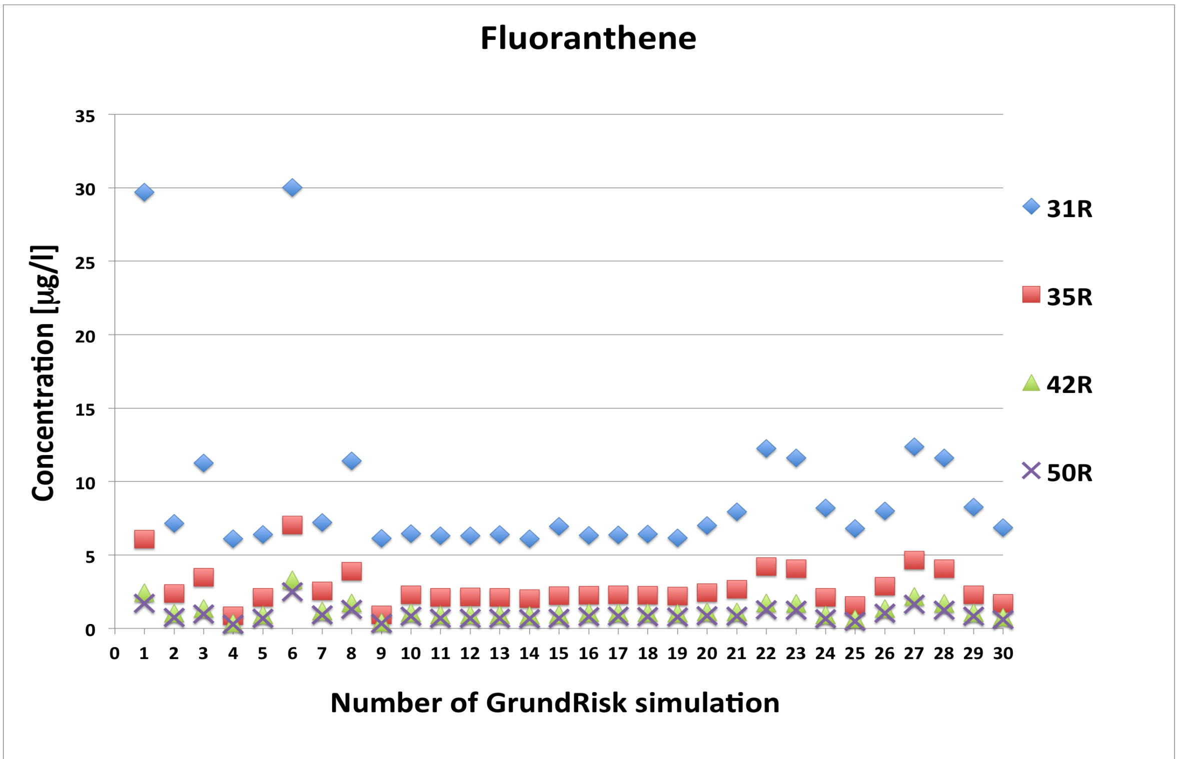
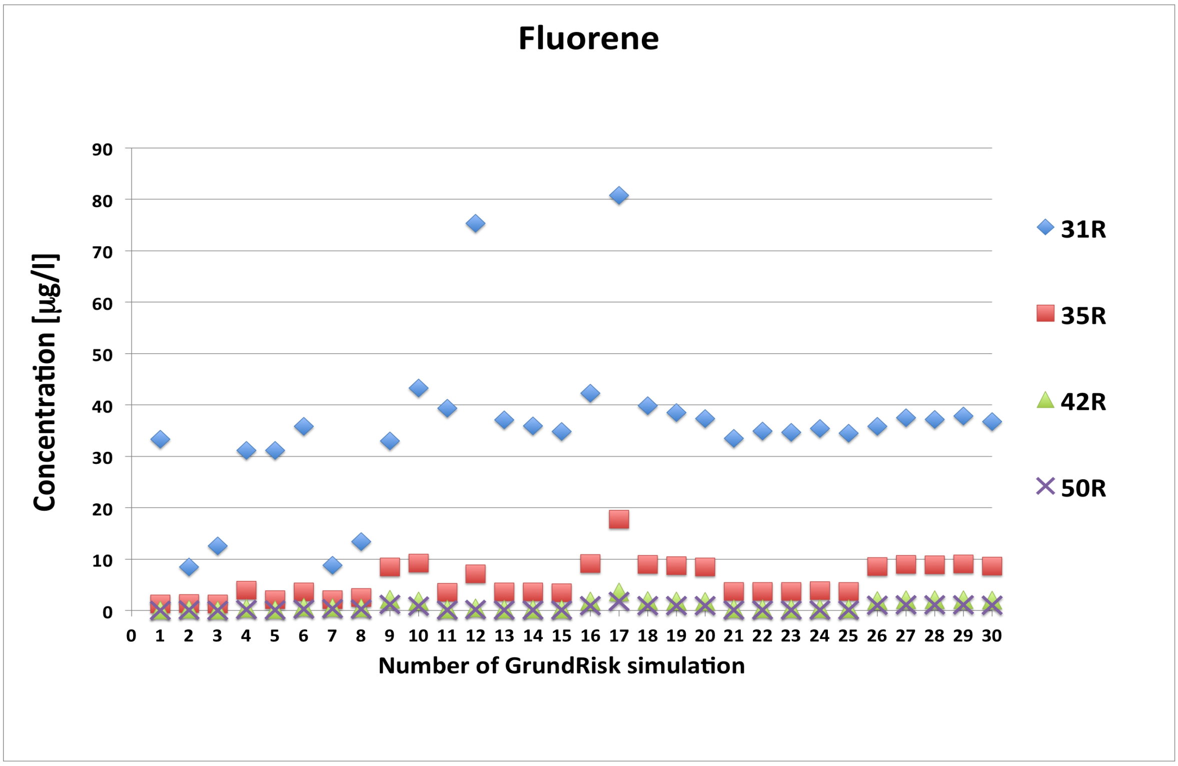


Figure 4: Anthracene and Fluoranthene concentrations obtained in each of the 30 GrundRisk simulations for well 31R, 35R, 42R and 50R. All the results are below the groundwater guidelines, i.e., for respectively Anthracene and Fluoranthene, 2000 and 300 μg/l. The number of the simulation is on the x-axis, and each point of the graph is the concentration obtained for the well in the simulation



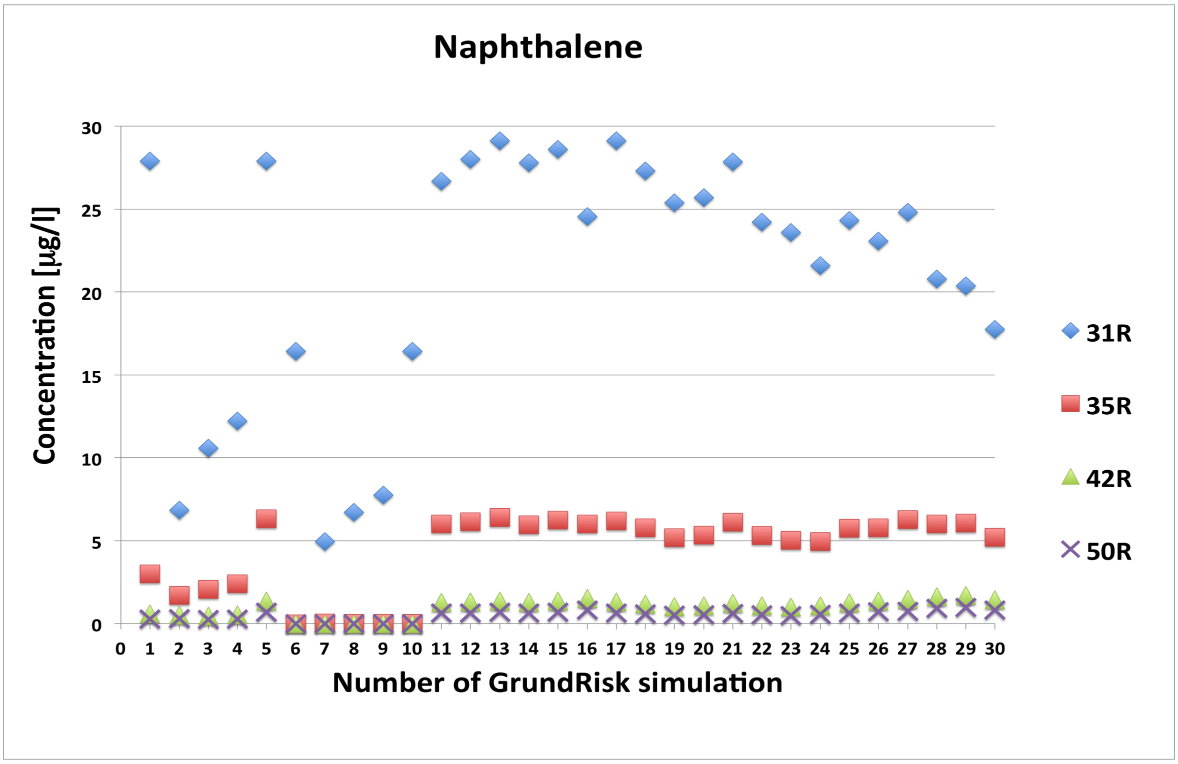
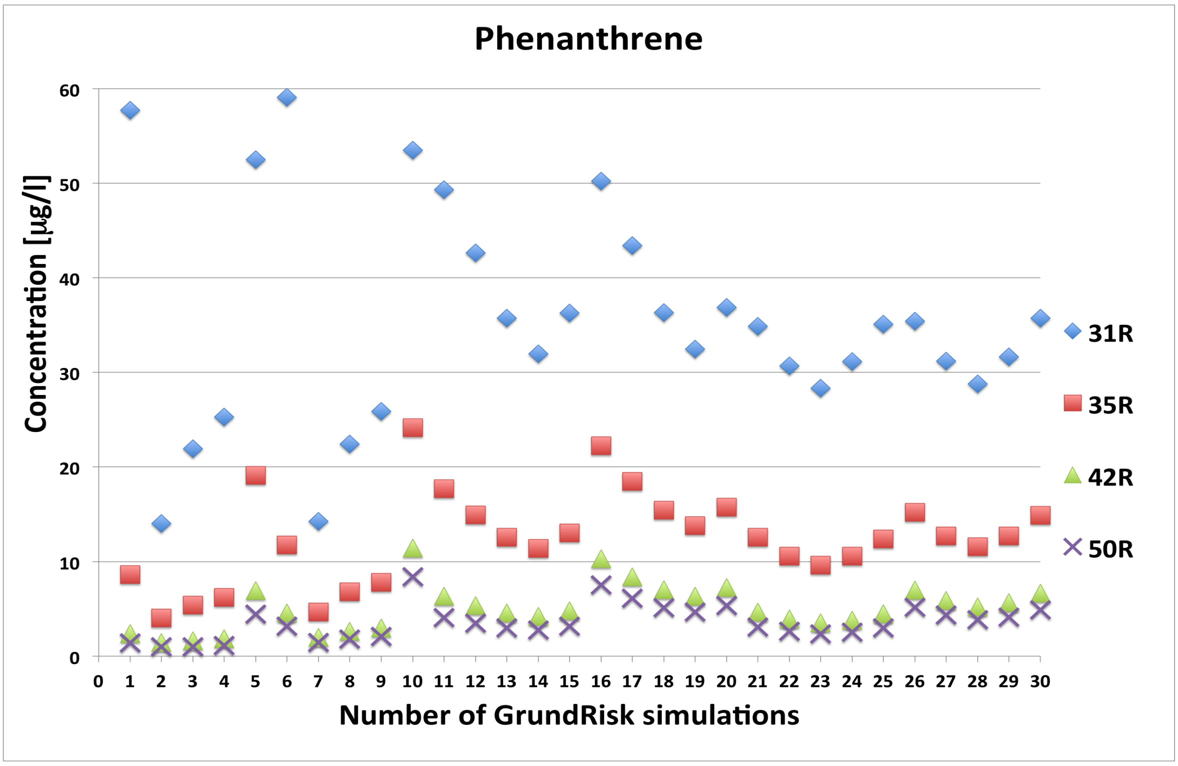


Figure 5: Fluorene and Naphthalene concentrations obtained in each of the 30 GrundRisk simulations for well 31R, 35R, 42R and 50R. All the results are below the groundwater guidelines, i.e., for both Fluorene and Naphthalene, 300 μg/l. The number of the simulation is on the x-axis, and each point of the graph is the concentration obtained for the well in the simulation



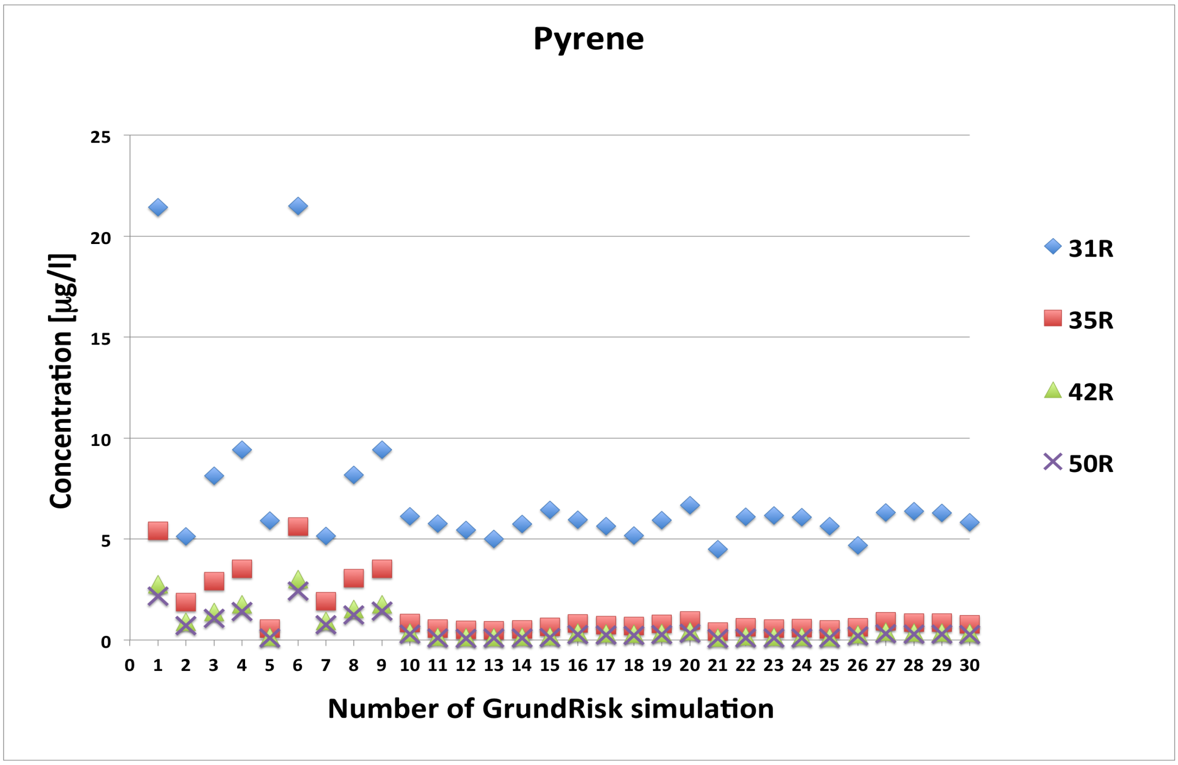


Figure 6: Phenanthrene and Pyrene concentrations obtained in each of the 30 GrundRisk simulations for well 31R, 35R, 42R and 50R. All the results are below the groundwater guidelines, i.e., for respectively Phenanthrene and Pyrene, 100 and 200 μg/l. The number of the simulation is on the x-axis, and each point of the graph is the concentration obtained for the well in the simulation

Appendix 4 - Calculation of human health risks

Default parameters

Table 6: Body Weight (BW), Exposure Dose (ED), Exposure Factor (EF), Exposure Time (ET) and Intake Rate (IR) default values [111]

Parameter	Male	Female
BW - infant (6 < 12 months) [kg]	9.4	9.0
BW- child (2 < 3 years) [kg]	14.1	13.5
BW- child (3 < 6 years) [kg]	18.8	18.3
BW- child (6 < 11 years) [kg]	31.9	31.7
BW- child (11 < 16 years) [kg]	57.6	55.9
BW- child (16 < 21 years) [kg]	77.3	65.9
BW - adult (> 21 years) [kg]	85.9	73.3
ED - lifetime [year]	70	70
EF - daily [-]	1	1
ET shower -child & infant [min/day]	20	20
ET shower - adult [min/day]	12	12
IR - infant and child [liter/day]	1	1
IR - adult [liter/day]	2	2

Table 7: Body Surface Area (BSA) default values [111]

Age	Male [cm^2]	Female [cm^2]
6 < 12 months	4500	4400
2 < 3 years	6100	6000
3 < 6 years	7600	7500
6 < 11 years	10800	10800
11 < 16 years	15900	15700
16 < 21 years	18400	17300
> 21 years	19200	16900

Results of the human health risk assessment on Chlorophenols (CPs)

Table 8: Males, exposure dose D from ingestion, for a daily exposure, of water containing Chlorophenols (CPs) for different exposure factors EFs. The value is highlighted in red if it is above the reference dose RfD

Males, ingestion exposure D [mg/kg/day] for F = 30 days (EF = 0.08)

Chemical	$RfD_{Ingestion}$ [mg/kg/day]	D, infant (6 < 12 months)	D, child (6 < 11 years)	D, adult (> 21 years)
2-CP	5.0E-03	3.4E-03	1.0E-03	7.5E-04
2,4-DCP	3.0E-03	2.5E-03	7.4E-04	5.5E-04
2,3,4,6-TeCP	3.0E-02	8.7E-01	2.6E-01	1.9E-01
PCP	5.0E-03	2.1E-02	6.2E-03	4.6E-03

Males, ingestion exposure [mg/kg/day] for F = 104 days (EF = 0.28)

Chemical	$RfD_{Ingestion}$ [mg/kg/day]	D, infant (6 < 12 months)	D, child (6 < 11 years)	D, adult (> 21 years)
2-CP	5.0E-03	1.2E-02	3.5E-03	2.6E-03
2,4-DCP	3.0E-03	8.7E-03	2.6E-03	1.9E-03
2,3,4,6-TeCP	3.0E-02	3.1E+00	9.0E-01	7.0E-01
PCP	5.0E-03	7.3E-02	2.1E-02	1.6E-02

Males, ingestion exposure [mg/kg/day] for F = 208 days (EF = 0.57)

Chemical	$RfD_{Ingestion}$	D, infant (6 < 12 months)	D, child (6 < 11 years)	D, adult (> 21 years)
2-CP	5.0E-03	2.4E-02	7.0E-03	5.2E-03
2,4-DCP	3.0E-03	1.7E-02	5.1E-03	3.8E-03
2,3,4,6-TeCP	3.0E-02	6.1E+00	1.8E+00	1.3E+00
PCP	5.0E-03	0.1	4.3E-02	3.2E-02

Table 9: Males, exposure dose D from dermal contact, for a daily exposure (EF =1), with water containing Chlorophenols (CPs). The value is highlighted in red if it is above the reference dose RfD

Males, dermal exposure D [mg/kg/day] for a shower taken every day of the year (EF = 1)

Chemical	RfD_{Dermal} [mg/kg/day]	D, infant (6 < 12 months)	D, child (6 < 11 years)	D, adult (> 21 years)
2-CP	4.0E-03	4.5E-04	3.2E-04	1.4E-04
2,4-DCP	2.5E-03	8.7E-04	6.1E-04	2.7E-04
PCP	3.8E-03	1.3E-01	1.0E-01	4.0E-02

Table 10: Males, Hazard Quotient HQ given the intakes through a daily ingestion and a daily dermal contact of Chlorophenols (CPs). The value is highlighted in red if it is above the acceptable level of 1

HQ Ingestion [-]

Chemical	**D, infant ($6 < 12$ months)**	**D, child ($6 < 11$ years)**	**D, adult (> 21 years)**
2-CP	8.3E+00	2.5E+00	1.8E+00
2,4-DCP	1.0E+01	3.0E+00	2.2E+00
2,3,4,6-TeCP	3.5E+02	1.0E+02	7.7E+01
PCP	5.1E+01	1.5E+01	1.1E+01

HQ Dermal [-]

Chemical	**D, infant ($6 < 12$ months)**	**D, child ($6 < 11$ years)**	**D, adult (> 21 years)**
2-CP	1.1E-01	8.0E-02	3.5E-02
2,4-DCP	3.5E-01	2.5E-01	1.1E-01
PCP	3.5E+01	2.5E+01	1.1E+01

Table 11: Males, Hazard Index HI given by the sum of the intakes of each Chlorophenol (CP) for a daily ingestion and a daily dermal contact. The value is highlighted in red if it is above the acceptable level of 1

$$\mathbf{HI} = \Sigma \mathbf{HQ}_{Chemical} \ [\text{-}]$$

Group of people	**HI Ingestion [-]**	**HI Dermal [-]**
D, infant ($6 < 12$ months)	4.2E+02	3.6E+01
D, child ($6 < 11$ years)	1.2E+02	2.5E+01
D, adult (> 21 years)	9.3E+01	1.1E+01

Results of the human health risk assessment on Polycyclic Aromatic Hydrocarbons (PAHs) in well 31R

Table 12: Males, exposure dose D from ingestion, for a daily exposure, of water containing Polycyclic Aromatic Hydrocarbons (PAHs), for different exposure factors EFs, detected in well 31R - first part

Males, ingestion dose [mg/kg/day] for F = 30 days (EF = 0.08)

Chemical	**RfD**$_{Ingestion}$	**D, infant (6 < 12 months)**	**D, child (6 < 11 years)**	**D, adult (> 21 years)**
Acenaphthene	6.0E-02	1.6E-03	4.8E-04	3.6E-04
Anthracene	3.0E-01	1.0E-04	2.8E-05	2.1E-05
Benzo(a)pyrene	3.0E-04	1.7E-05	5.1E-06	3.8E-06
Fluoranthene	4.0E-02	2.6E-04	7.7E-05	5.7E-05
Fluorene	4.0E-02	7.1E-04	2.1E-04	1.5E-04
Naphthalene	2.0E-02	2.5E-04	7.5E-05	5.6E-05
Pyrene	3.0E-02	1.9E-04	5.5E-05	4.1E-05

Males, ingestion dose [mg/kg/day] for F = 104 days (EF = 0.28)

Chemical	**RfD**$_{Ingestion}$	**D, infant (6 < 12 months)**	**D, child (6 < 11 years)**	**D, adult (> 21 years)**
Acenaphthene	6.0E-02	5.6E-03	1.7E-03	51.2E-03
Anthracene	3.0E-01	3.3E-04	1.0E-04	7.3E-05
Benzo(a)pyrene	3.0E-04	6.0E-05	1.8E-05	1.3E-05
Fluoranthene	4.0E-02	9.1E-04	2.7E-04	2.0E-04
Fluorene	4.0E-02	2.4E-03	7.2E-04	5.4E-04
Naphthalene	2.0E-02	8.8E-04	2.6E-04	1.9E-04
Pyrene	3.0E-02	6.5E-04	1.9E-04	1.4E-04

Table 13: Males, exposure dose D from ingestion, for a daily exposure, of water containing Polycyclic Aromatic Hydrocarbons (PAHs) detected in well 31R for different exposure factors EFs - second part

Males, ingestion exposure [mg/kg/day] for F = 208 days (EF = 0.57)

Chemical	**RfD**$_{Ingestion}$	**D, infant (6 < 12 months)**	**D, child (6 < 11 years)**	**D, adult (> 21 years)**
Acenaphthene	6.0E-02	1.1E-02	3.3E-03	2.5E-03
Anthracene	3.0E-01	6.7E-04	2.0E-04	1.5E-04
Benzo(a)pyrene	3.0E-04	1.2E-04	3.5E-05	2.6E-05
Fluoranthene	4.0E-02	1.8E-03	5.4E-04	4.0E-04
Fluorene	4.0E-02	4.9E-03	1.4E-03	1.1E-03
Naphthalene	2.0E-02	1.8E-03	5.2E-04	3.9E-04
Pyrene	3.0E-02	1.3E-03	3.8E-04	2.9E-04

Males, ingestion exposure [mg/kg/day] for a daily exposure (EF = 1)

Chemical	**RfD**$_{Ingestion}$	**D, infant (6 < 12 months)**	**D, child (6 < 11 years)**	**D, adult (> 21 years)**
Acenaphthene	6.0E-02	2.0E-02	5.8E-03	4.3E-03
Anthracene	3.0E-01	1.2E-03	3.5E-04	2.6E-04
Benzo(a)pyrene	3.0E-04	2.1E-04	6.2E-05	4.6E-05
Fluoranthene	4.0E-02	3.2E-03	9.4E-04	7.0E-04
Fluorene	4.0E-02	8.6E-03	2.5E-03	1.9×10^{-3}
Naphthalene	2.0E-02	3.1E-03	9.1E-04	6.8E-04
Pyrene	3.0E-02	2.3E-03	6.7E-04	5.0E-04

Table 14: Males, exposure dose D from dermal contact, for a daily exposure (EF =1), with water containing Polycyclic Aromatic Hydrocarbons (PAHs) detected in well 31R. The value is highlighted in red if it is above the reference dose RfD

Males, dermal exposure D [mg/kg/day] for a shower taken every day of the year (EF = 1)

Chemical	**RfD**$_{Dermal}$	**D, infant (6 < 12 months)**	**D, child (6 < 11 years)**	**D, adult (> 21 years)**
Benzo(a)pyrene	2.7E-04	2.0E-04	1.4E-04	6.2E-05
Fluoranthene	3.6E-02	9.5E-04	6.7E-04	3.0E-04
Naphthalene	1.8E-02	2.0E-04	1.4E-04	6.1E-05

Table 15: Males, Hazard Quotient HQ given by the intakes through a daily ingestion and a daily dermal contact of Polycyclic Aromatic Hydrocarbons (PAHs) detected in well 31R. The value is highlighted in red if it is above the acceptable level of 1

HQ Ingestion [-]

Chemical	**D, infant ($6 < 12$ months)**	**D, child ($6 < 11$ years)**	**D, adult (> 21 years)**
Acenaphthene	3.0E-01	1.0E-01	7.0E-02
Anthracene	4.0E-03	1.2E-03	9.0E-04
Benzo(a)pyrene	7.0E-01	2.0E-01	2.0E-01
Fluoranthene	8.0E-02	2.4E-02	1.7E-02
Fluorene	2.0E-01	6.0E-02	5.0E-02
Naphthalene	2.0E-01	4.6E-02	3.4E-02
Pyrene	7.6E-02	2.2E-02	1.7E-02

HQ Dermal [-]

Chemical	**D, infant ($6 < 12$ months)**	**D, child ($6 < 11$ years)**	**D, adult (> 21 years)**
Benzo(a)pyrene	7.0E-01	5.0E-01	2.0E-01
Fluoranthene	2.6E-02	1.9E-02	8.0E-03
Naphthalene	1.1E-02	8.0E-03	3.0E-03

Table 16: Males, Hazard Index HI given by the sum of the intakes of each Polycyclic Aromatic Hydrocarbon (PAH), detected in well 31R, for a daily ingestion exposure and a daily dermal contact. The value is highlighted in red if it is above the acceptable level of 1

$\mathbf{HI} = \Sigma \mathbf{HQ}_{Chemical}$ [-]

Group of people	**HI Ingestion [-]**	**HI Dermal [-]**
D, infant ($6 < 12$ months)	1.6	0.8
D, child ($6 < 11$ years)	0.5	0.5
D, adult (> 21 years)	0.3	0.2

Results of the human health risk assessment on Polycyclic Aromatic Hydrocarbons (PAHs) in well 50R

Table 17: Males, exposure dose D from ingestion, for a daily exposure, of water containing Polycyclic Aromatic Hydrocarbons (PAHs) detected in well 50R for different exposure factors EFs

Males, ingestion exposure [mg/kg/day] for a daily exposure (EF = 1)

Chemical	**RfD**	**D, infant (6 < 12 months)**	**D, child (6 < 11 years)**	**D, adult (> 21 years)**
Acenaphthene	6.0E-02	1.3E-03	3.7E-04	2.7E-04
Anthracene	3.0E-01	2.7E-04	7.8E-05	5.8E-05
Benzo(a)pyrene	3.0E-04	2.4E-05	7.2E-06	5.4E-06
Fluoranthene	4.0E-02	2.7E-04	7.8E-05	5.8E-05
Fluorene	4.0E-02	1.9E-04	5.6E-05	4.2E-05
Naphthalene	2.0E-02	9.6E-05	2.8E-05	2.1E-05
Pyrene	3.0E-02	2.6E-04	7.5E-05	5.6E-05

Table 18: Males, exposure dose D from dermal contact, for a daily exposure (EF =1), with water containing Polycyclic Aromatic Hydrocarbons (PAHs) detected in well 50R, i.e. the point of compliance in the GrundRisk simulations

Males, dermal exposure D [mg/kg/day] for a shower taken every day of the year (EF = 1)

Chemical	**RfD**$_{Dermal}$	**D, infant (6 < 12 months)**	**D, child (6 < 11 years)**	**D, adult (> 21 years)**
Benzo(a)pyrene	2.7E-04	2.3E-05	1.6E-05	7.2E-06
Fluoranthene	3.6E-02	7.9E-05	5.6E-05	2.5E-05
Naphthalene	1.8E-02	6.1E-06	4.3E-06	1.9E-06

Table 19: Males, Hazard Quotient HQ, of Polycyclic Aromatic Hydrocarbons (PAHs) detected in well 50R (the point of compliance in the GrundRisk simulations) given by the intakes through a daily ingestion exposure and a daily dermal contact

HQ Ingestion [-]

Chemical	**D, infant (6 < 12 months)**	**D, child (6 < 11 years)**	**D, adult (> 21 years)**
Acenaphthene	2.1E-02	6.2E-03	4.6E-03
Anthracene	9.0E-04	3.0E-04	2.0E-04
Benzo(a)pyrene	8.2E-02	2.4E-02	1.8E-02
Fluoranthene	6.6E-03	2.0E-03	1.5E-03
Fluorene	4.8E-03	1.4E-03	1.0E-03
Naphthalene	4.8E-03	1.4E-03	1.0E-03
Pyrene	8.5E-03	2.5E-03	1.9E-03

HQ Dermal [-]

Chemical	**D, infant (6 < 12 months)**	**D, child (6 < 11 years)**	**D, adult (> 21 years)**
Benzo(a)pyrene	8.6E-02	6.1E-02	2.7E-02
Fluoranthene	2.2E-03	1.6E-03	7.0E-04
Naphthalene	3.0E-04	2.0E-04	1.0E-04

Table 20: Males, Hazard Index HI given by the sum of the intakes of each Polycyclic Aromatic Hydrocarbon (PAH), detected in well 50R (the point of compliance in the GrundRisk simulations), for a daily ingestion exposure and for a daily dermal contact

$$\mathbf{HI} = \Sigma \mathbf{HQ}_{Chemical} \text{ [-]}$$

Group of people	**HI Ingestion [-]**	**HI Dermal [-]**
D, infant (6 < 12 months)	1.3E-01	9.0E-02
D, child (6 < 11 years)	3.8E-02	6.0E-02
D, adult (> 21 years)	2.8E-02	3.0E-02

Results of the human health risk assessment on Polycyclic Aromatic Hydrocarbons (PAHs) in the source area in the aquifer

Table 21: Males, exposure dose D from ingestion, for a daily exposure, of water containing Polycyclic Aromatic Hydrocarbons (PAHs) detected in the source area in the aquifer. for different exposure factors EFs. The value is highlighted in red if it is above the reference dose RfD

Males, ingestion exposure [mg/kg/day] for a daily exposure (EF = 1)

Chemical	RfD	D, infant (6 < 12 months)	D, child (6 < 11 years)	D, adult (> 21 years)
Acenaphthene	6.0E-02	2.0E-01	5.0E-02	3.0E-02
Anthracene	3.0E-01	2.0E-02	1.0E-02	4.0E-03
Benzo(a)pyrene	3.0E-04	1.0E-02	2.0E-03	1.0E-03
Fluoranthene	4.0E-02	1.0E-01	3.0E-02	2.0E-02
Fluorene	4.0E-02	1.0E-01	3.0E-02	2.0E-02
Naphthalene	2.0E-02	1.0E-01	3.0E-02	2.0E-02
Pyrene	3.0E-02	6.0E-02	2.0E-02	1.0E-02

Table 22: Males, exposure dose D from dermal contact, for a daily exposure (EF =1), with water containing Polycyclic Aromatic Hydrocarbons (PAHs) detected in the source area in the aquifer. The value is highlighted in red if it is above the reference dose RfD

Males, dermal exposure D [mg/kg/day] for a shower taken every day of the year (EF = 1)

Chemical	RfD_{Dermal}	D, infant (6 < 12 months)	D, child (6 < 11 years)	D, adult (> 21 years)
Benzo(a)pyrene	2.7E-04	5.4E-03	3.8E-03	1.7E-03
Fluoranthene	3.6E-02	2.6E-02	1.8E-02	8.1E-03
Naphthalene	1.8E-02	5.5E-03	3.9E-02	1.7E-03

Table 23: Males, Hazard Quotient HQ given by the intakes of Polycyclic Aromatic Hydrocarbons (PAHs), detected in the source area in the aquifer, for a daily ingestion exposure and for a daily dermal contact. The value is highlighted in red if it is above the acceptable level of 1

HQ Ingestion [-]

Chemical	**D, infant (6 < 12 months)**	**D, child (6 < 11 years)**	**D, adult (> 21 years)**
Acenaphthene	2.6E+00	8.0E-01	6.0E-01
Anthracene	6.4E-02	1.9E-02	1.4E-02
Benzo(a)pyrene	1.9E+01	5.6E+00	4.2E+00
Fluoranthene	2.2E+00	6.0E-01	5.0E-01
Fluorene	2.8E+00	8.0E-01	6.0E-01
Naphthalene	4.3E+00	1.3E+00	9.0E-01
Pyrene	2.1E+00	6.0E-01	5.0E-01

HQ Dermal [-]

Chemical	**D, infant (6 < 12 months)**	**D, child (6 < 11 years)**	**D, adult (> 21 years)**
Benzo(a)pyrene	2.0E+01	1.4E+01	6.3E+00
Fluoranthene	7.0E-01	5.0E-01	9.0E-01
Naphthalene	3.0E-01	2.0E-01	1.0E-01

Table 24: Males, Hazard Index HI given by the sum of the intakes of each Polycyclic Aromatic Hydrocarbon (PAH), detected in the source area in the aquifer, for a daily ingestion exposure and for a daily dermal contact. The value is highlighted in red if it is above the acceptable level of 1

$$\mathbf{HI} = \Sigma \mathbf{HQ}_{Chemical} \ [-]$$

Group of people	**HI Ingestion [-]**	**HI Dermal [-]**
D, infant (6 < 12 months)	3.3E+01	2.1E+01
D, child (6 < 11 years)	9.8E+00	1.5E+01
D, adult (> 21 years)	7.3E+00	7.3E+00